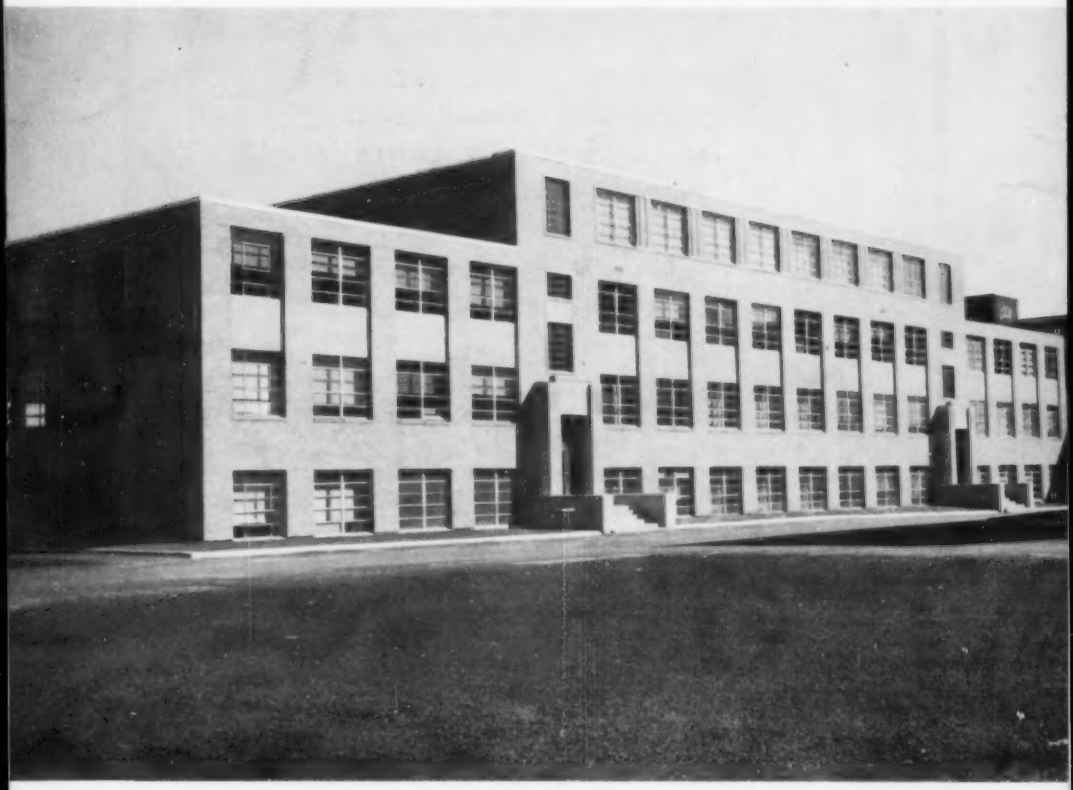
THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. LII MAY 1957 No. 5



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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LII MAY 1957 No. 5

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Cover—Olney Hall, Lowell Technological Institute

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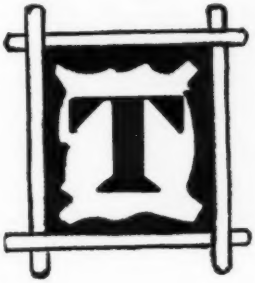

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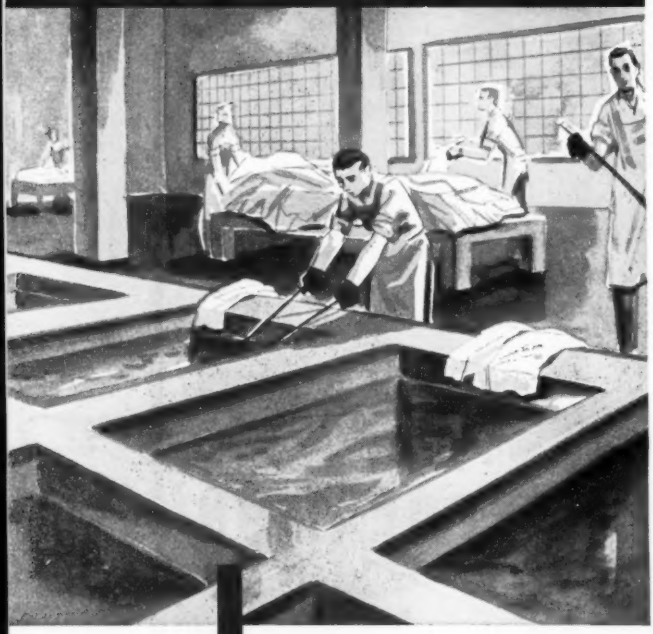

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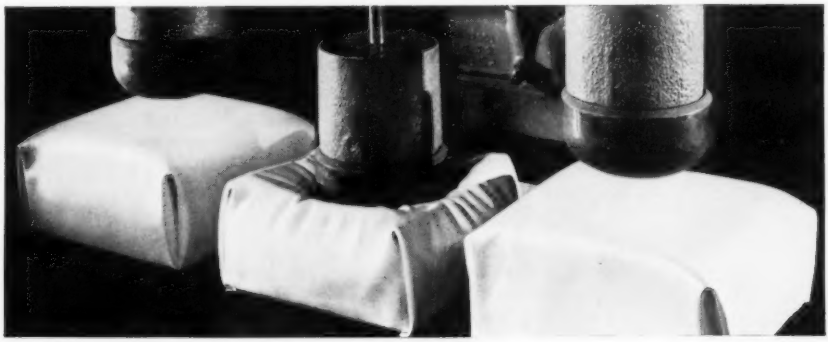

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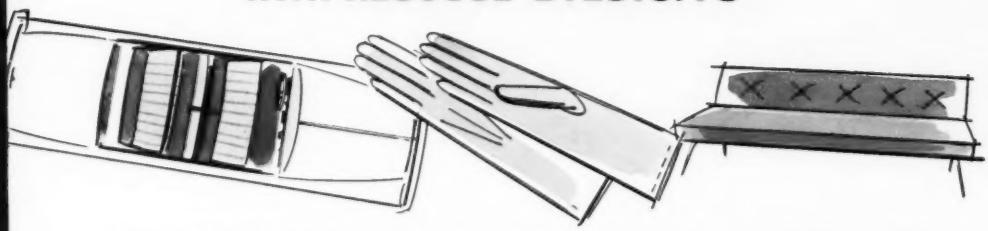

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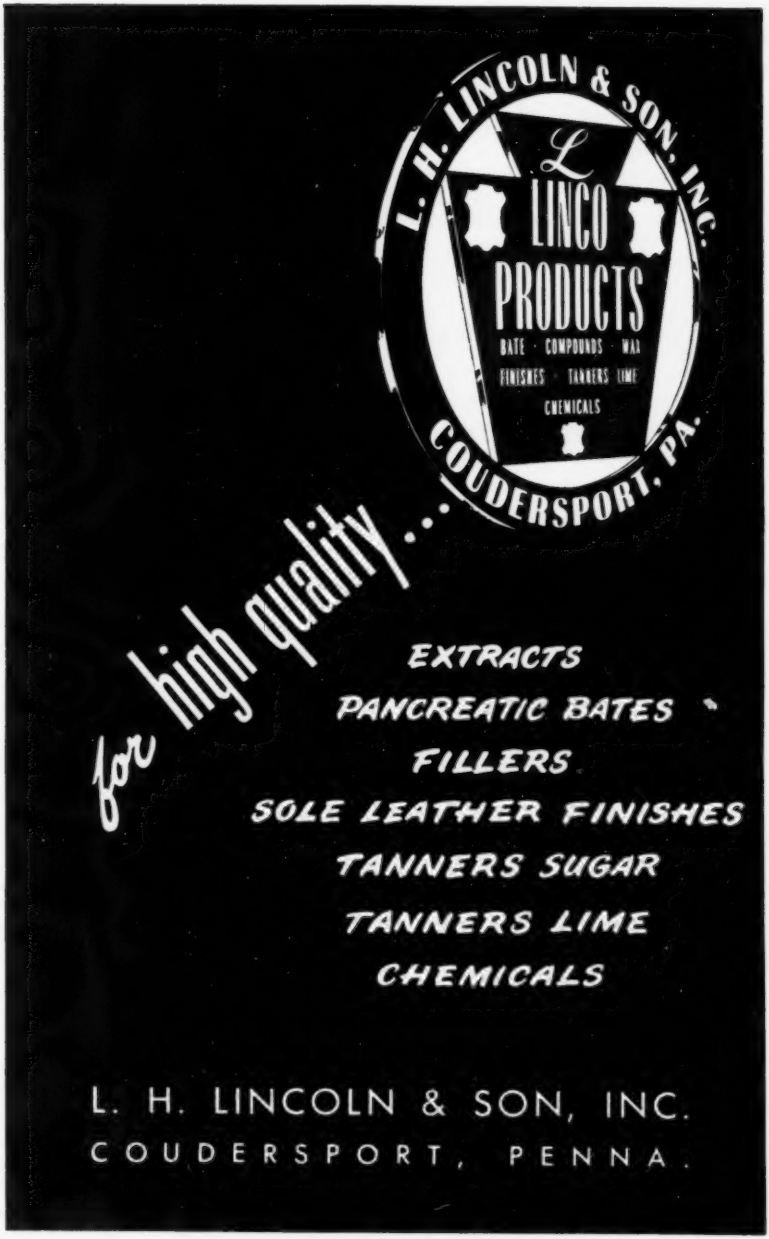
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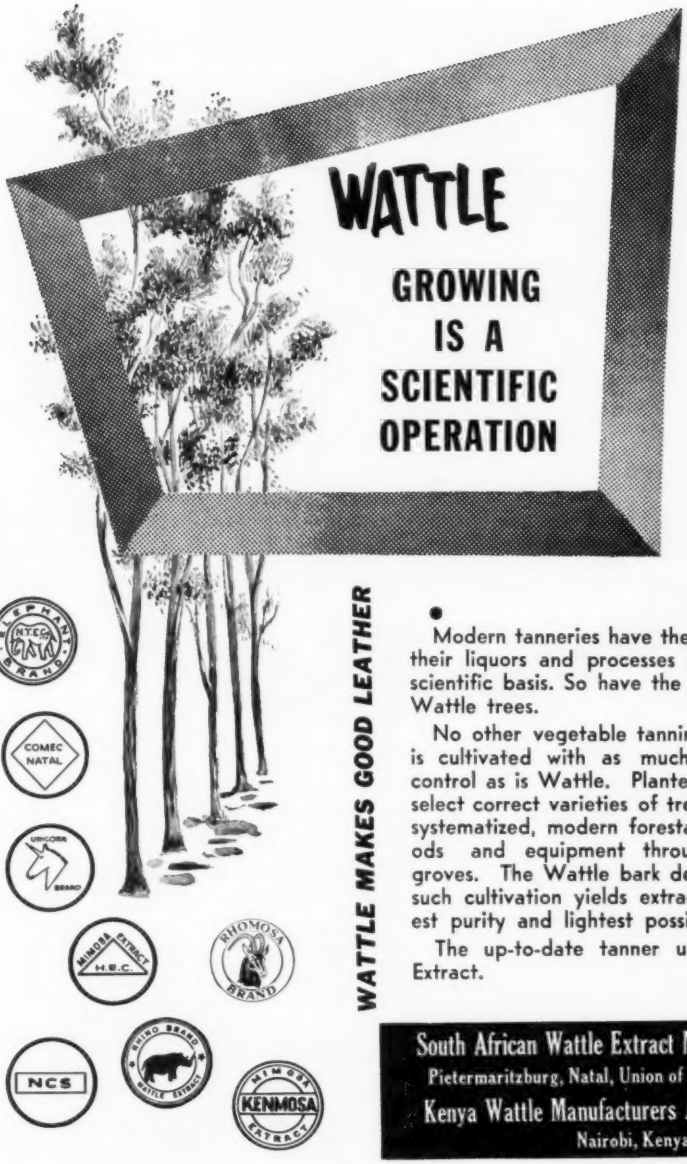

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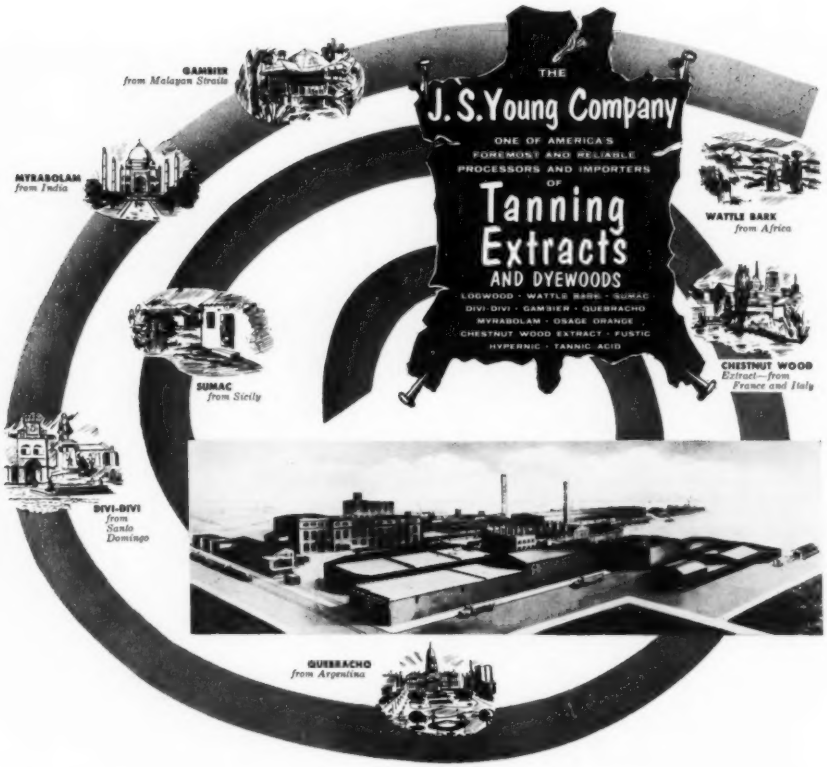

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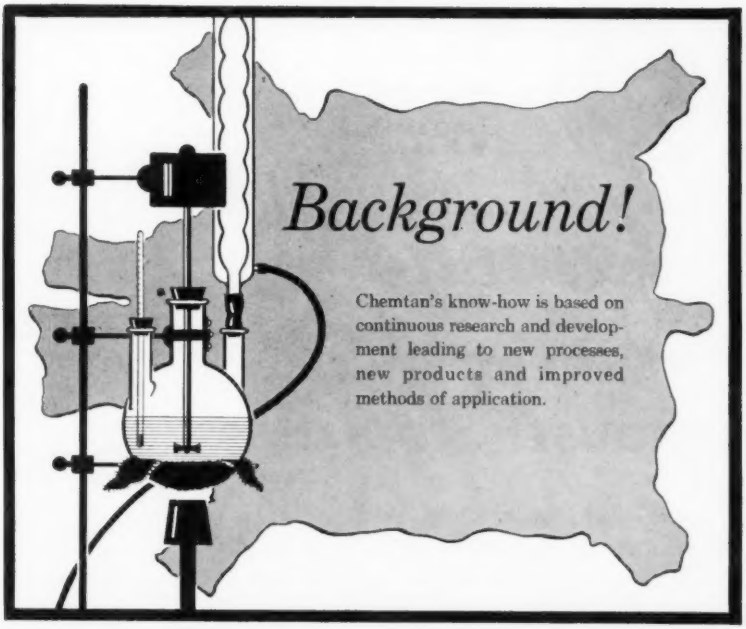
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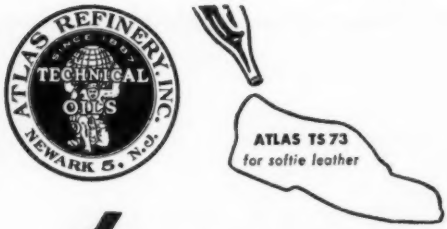

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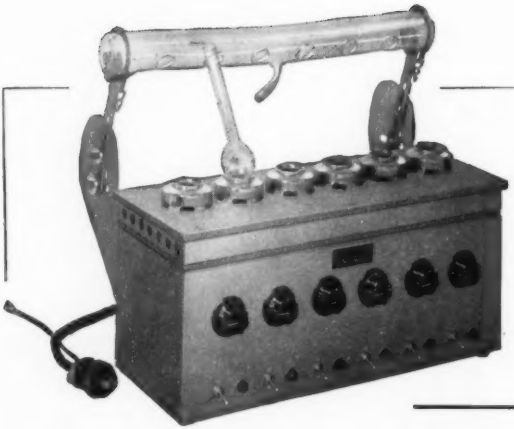

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THE EFFECT OF SALTS IN FORMALDEHYDE TANNAGE. I.

Y. Nayudamma, S. K. Jayaraman, and T. S. Krishnan

Central Leather Research Institute
Madras, India

ABSTRACT

Collagen pieces were tanned with formaldehyde at pH 7 in the presence of equimolecular quantities of 20 different salts. In general the presence of salt raised the fixation of formaldehyde and the shrink temperature. Three of the more effective salts were used at different concentrations at pH 7, and at constant concentration at pH values from 2 to 11. These salts caused increased fixation at pH values below 3.5 and above 5, and decreased fixation at pH 3.5–5.

ABSTRACTO

Piezas colágenas fueron curtidas con un formaldehido a un pH de 7 en presencia de la misma cantidad molecular de 20 sales diferentes. En general, la presencia de una sal subió la fijación del formaldehido y la temperatura del encoge. Tres de las sales más efectivas fueron usadas a diferentes concentraciones a un pH de 7, y a una concentración constante con valores de pH entre 2 y 11. Estas sales causaron un aumento en la fijación a valores de pH menores de 3.5 y mayores de 5, y un decrecimiento en la fijación con un pH entre 3.5 y 5.

INTRODUCTION

While numerous researches have shown that neutral salts have a marked effect on tanning with chromium sulfate and vegetable tannins, very little work has been done with regard to the effect of salts on formaldehyde tannage. A number of workers (1–6) have suggested that the presence of salts during formaldehyde tannage prevents crackiness of the grain. Theis and Schaffer (4), taking shrinkage temperature as a measure of tanning, showed that sodium acetate, formate, and thiosulfate increased the degree of tannage appreciably but sodium sulfate only slightly, and that sodium chloride decreased the degree of tannage. In later publications, Theis *et al.* (7,8) reported that NaCl, KCl, and $CaCl_2$ increased the fixation of formaldehyde at any given pH value. Bowes and Pleass (5) found that collagen combined with

less formaldehyde, below the isoelectric point, in the presence of "universal buffer" (phenylacetic, phosphoric, and boric acid mixture) than in unbuffered solutions; above the isoelectric point more formaldehyde was fixed in the presence of the buffer. They also noted that addition of Na_2CO_3 decreased formaldehyde fixation at pH values below 9, and increased the fixation of pH values above 9. They state that the reason for these effects is obscure and suggest that a study of the effects of salts other than Na_2CO_3, and those contained in universal buffer, might clarify the situation.

A systematic study of the effects of salts on formaldehyde tanning therefore appears to be desirable and has been taken up in this laboratory. The effects of adding fixed amounts of 20 different salts of organic and inorganic acids on the amount of formaldehyde fixed when collagen is tanned with a fixed amount of formaldehyde have been studied, along with shrink temperatures and swelling of the resulting product. The effects of pH value and of salt concentration have been studied with certain of the more promising salts. The results are reported in this paper.

EXPERIMENTAL

Materials.—The collagen consisted of butt portions of wet-salted cowhides, soaked and limed in the traditional manner, fully delimed with acetic acid, washed free from salts, and dehydrated with alcohol and acetone.

Tanning procedure.—A known weight of collagen was thoroughly wet back with water, and tanned in 500 parts water containing 1% formaldehyde on the weight of collagen and the desired amount of salt. Immediately after placing the skin in the liquor, the pH value was brought to 7.0 by adding NaOH or HCl and was maintained by further additions of acid or alkali. After 4 days, a specimen was taken for determining shrink temperature. The rest of the material was washed with several changes of water previously adjusted to the pH of the tanning solution. Then the pieces were blotted between filter papers and weighed. The increase in weight was noted to calculate the degree of swelling, expressed as percentage increase in weight of the original dry, dehydrated pelt. The pieces were then dried in the air and analyzed for hide substance and bound aldehyde. The data for the effect of salts on fixed formaldehyde, shrink temperature, and swelling, for tannage at pH 7, are given in Table I.

RESULTS AND DISCUSSION

Fixed formaldehyde.—From Table I, in which the salts are listed in decreasing order of amount of formaldehyde fixed, it is clear that all the salts except $CaCl_2$, K_2SO_4, $AlCl_3$, and $Al_2(SO_4)_3$ increase the fixation of formaldehyde to a greater or lesser degree. In general, the salts of organic acids are more effective than inorganic salts, except $Na_2Cr_2O_7$.

TABLE I

EFFECT OF DIFFERENT SALTS ON FORMALDEHYDE TANNAGE

Salt	Fixed HCHO (meq/100g collagen)	Ts (°C.)	Swelling %
Sodium acetate	53.93	84.5	148
Magnesium acetate	53.57	91.0	128
Sodium dichromate	41.04	84.5	142
Sodium lactate	36.39	87.5	128
Sodium citrate	35.50	86.0	145
Sodium thiosulfate	34.63	83.0	138
Sodium chloride	34.20	83.0	120
Sodium phthalate	32.81	85.0	146
Sodium borate	31.84	86.5	140
Sodium oxalate	29.95	83.8	125
Sodium hexametaphosphate (Calgon)	29.76	82.0	138
Magnesium chloride	29.70	85.0	127
Sodium formate	29.59	84.0	136
Sodium tartrate	29.07	85.0	138
Sodium sulfate	28.78	82.0	125
Sodium sulfite	28.78	80.0	128
Control (no salt)	**27.01**	**80.3**	**140**
Calcium chloride	26.14	82.5	125
Potassium sulfate	25.96	81.5	128
Aluminum chloride	22.32	81.5	126
Aluminum sulfate	21.79	81.5	130

pH of tanning: 7.0.
500% float on dry pelt weight.
Amt. of salt added: 100 meq/100 g protein.
Formaldehyde: 1 g/100 g hide substance.

Considering only the inorganic salts, the highest value for fixed formaldehyde was recorded in the case of $Na_2Cr_2O_7$ addition—an increase of 50% over the control—followed by $Na_2S_2O_3$, NaCl, and $Na_2B_4O_7$. Fixation was decreased by $CaCl_2$, K_2SO_4, $AlCl_3$, and $Al_2(SO_4)_3$, by 20% in the last-named case. Since the tanning was done at pH 7, the basic aluminum salts formed may block some of the reactive groups of collagen, reducing the fixation of formaldehyde.*

Both the cation and the anion appear to have specific effects on formaldehyde fixation. Considering the anions, the order of decreasing effectiveness appears to be: dichromate – thiosulfate, chloride – borate – metaphosphate – sulfate, sulfite. The same order for the cations appears to be: sodium, potassium, magnesium, calcium, aluminum.

*It was pointed out to the authors that at pH 7 aluminum salts would be precipitated almost completely, so that the actual tannage was done in a suspension of $Al(OH)_3$ or insoluble basic salts, in a solution of NaCl or Na_2SO_4. The authors desire that the data for the aluminum salts be retained, because later experiments have shown that these salts also reduce formaldehyde fixation at lower pH values.—EDITOR.

All the organic salts studied increased the formaldehyde fixation. The decreasing order of effectiveness is: acetate, lactate, citrate, phthalate, oxalate, formate, tartrate. Among the salts studied, the acetates have an outstanding effect, increasing the fixation by 100% over the control. This applies to both sodium and magnesium acetates.

From this study it is clear that salts, in general, tend to increase the fixation of formaldehyde by collagen. Some inorganic salts tend to decrease the fixation, because of precipitation of hydroxides or reaction of basic metallic salts with collagen, reducing the number of active sites for reaction with formaldehyde. The exact mechanism for the increase in formaldehyde fixation in presence of salts is, however, not very clear. The increase in formaldehyde should be due to: (*a*) activation of the available groups to fix more formaldehyde for each group, (*b*) making more reactive groups available, and/or (*c*) making formaldehyde more reactive.

The effect of salts on dipolar ions like protein may be represented as follows:

The specific effect of ions depends upon their affinity, to the protein as compared to the water. According to Meyer and Dunkel (9) the affinity of Li^+ for $-NH_2$, -OH, and peptide groups of the protein is greater than its affinity to water, e.g., $PNH_2 + Li^+ \longrightarrow PNH_2Li^+$ (like PNH_3^+). Pfeiffer (10) showed that $-NH_2$ and -OH groups of amino acids, as well as protein, react with salts forming compounds like the addition compounds of salts with alcohols, ethers, etc.

It is well recognized that interaction between metal ions and proteins has an activating effect on a variety of enzymes. Similarly, the anion affinity for protein causes catalytic effect on the hydrolysis of amide and peptide bonds in acid solutions. Dilute solutions of neutral salts also tend to increase the stability of proteins. The effect of a salt is thus the sum of the effects of both the cation and anion, sometimes salting in and sometimes salting out the protein.

It has been established (11) that, in titrating a protein, at any given pH, the number of basic groups discharged will be greater in the presence of salts than in their absence. With the increase in the number of basic groups, a greater amount of formaldehyde is fixed, as observed in this study. But why certain ions are more effective than others is still obscure. The highest increase in formaldehyde was recorded with the addition of sodium acetate. The probable mechanism for this increase may be as follows: Sodium acetate,

the salt of a weak acid and strong base, hydrolyzes readily; the liberated NaOH reacts with the protein $-NH_3^+$ to yield $-NH_2$, which, in turn, readily reacts with formaldehyde.

$$Na\ AC + H_2O \longrightarrow NaOH + HAC$$

$$HAC + NaOH \longrightarrow Na\ AC.$$

To maintain the pH at 7.0, small amounts of alkali are added which will neutralize the acetic acid liberated, forming sodium acetate which, in turn, keeps on hydrolyzing.

The reactivity of formaldehyde may also be modified and increased. Thuau (15) observed that the tanning effect of formaldehyde was increased by the salts which bring about polymerization of HCHO, the resulting compound being absorbed by the hide.

More work is, however, desirable before definite postulates can be made in regard to the specific effects of cations, anions, carboxyl and hydroxyl groups, and the chain length of the acid on the fixation of formaldehyde by collagen. Studies of the formaldehyde reaction in the presence of salts of saturated and unsaturated acids, and aliphatic and aromatic acids; of the effect of salts like acetate on the individual amino acids, simple peptides, and proteins; and of the fixation of acetate by the protein and the formaldehyde fixed in the presence of acetate, may throw further light on this problem. Such studies are in progress.

Shrinkage temperature.—In every case, except possibly sodium sulfite, the presence of salts during tannage increased the shrinkage temperature of the resulting leather. It is apparent from Table I that the shrink temperature increases, in a general way, with increase in fixed formaldehyde, but there are many exceptions. Thus, formaldehyde fixation in the presence of sodium and magnesium acetates is practically the same, but the shrink temperature is 6.5° higher in the latter case. At the opposite end of the list, calcium

chloride, potassium sulfate, and the two aluminum salts all give shrink temperatures that are higher than that of the control, although the amount of fixed formaldehyde is lower.

Swelling.—The presence of salts reduces the swelling slightly in most cases. In a few instances (sodium borate, dichromate, acetate, citrate, and phthalate) the swelling is equal to, or slightly higher than, that of the control. The lowest swelling was obtained with sodium chloride. No very pronounced effect of salts on swelling would be anticipated when tanning at pH 7.

Effect of concentration of salt.—The effect of varying the concentration of certain salts (sodium citrate, sodium lactate, and magnesium acetate) was studied. The ratios of skin to liquor, and of formaldehyde to skin, and pH value, were the same as in the preceding experiments, but the concentrations of the salts were varied from 0.25 to 5 g. per 100 ml. The effects of salt concentration on fixed formaldehyde, percentage swelling, and shrink temperature are shown in Figure 1.

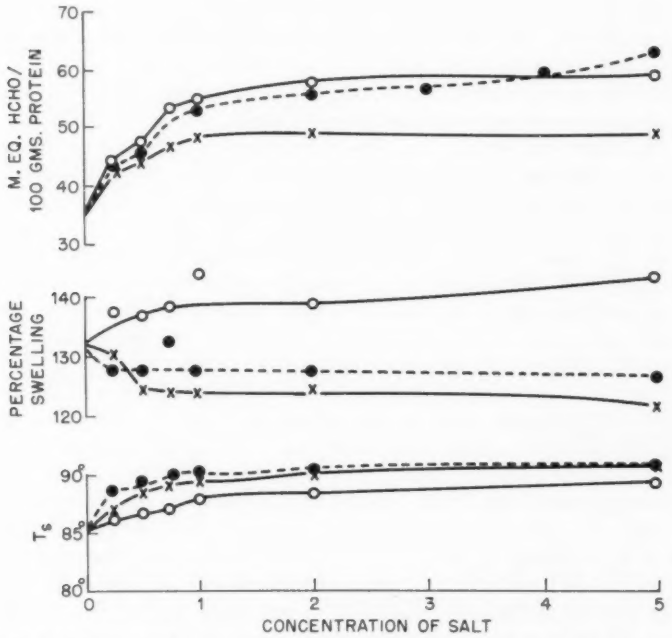

FIGURE 1.—Effect of salt concentration on fixation of formaldehyde, swelling, and shrink temperature, when tanning at pH 7.0.

X—X—X Na lactate; O—O—O Na citrate; ●—●—● Mg acetate.

With each salt, formaldehyde fixation increases with salt concentration, the rate of increase being most marked for concentrations up to 1% and the effects of the citrate and acetate being considerably greater than that of the lactate. The effects on shrinkage temperature are smaller, and the shrink temperature is increased more, in the presence of lactate than of citrate, which is the reverse of the effect on formaldehyde fixation. Swelling is increased by citrate, but decreased by acetate and lactate.

Effect of pH value.—The effects of varying the equilibrium pH value from 2.0 to 11.6 were studied, using 5% by volume of sodium acetate, sodium lactate, and magnesium acetate. The results are recorded in Figure 2. In the curve for the control (no added salt), formaldehyde fixation increases up to pH 6, shows a plateau in the range from 6 to 7, and increases sharply at higher pH values. These results agree closely with those of earlier workers. In the presence of salts, as compared to the control, fixation is the same, or a little greater, at pH 2.0–3.0, smaller at pH 3.5–5.0, and greater at all higher pH values. In the case of magnesium acetate, there are plateaus between pH 4.0 and 6.0 and between pH 8.0 and 9.5. Sodium acetate shows the second, but not the first, plateau. For sodium lactate, the increase of fixation with pH is almost linear.

The increase in fixed formaldehyde in the acid zone (pH 2.0–3.5) may be due to the reaction of formaldehyde with amide groups. Wormel and Kaye (12) reported that presence of salts is necessary to promote the reaction of formaldehyde with amide groups of casein, but this finding could not be confirmed by Fraenkel-Conrat *et al.* (13). Nayudamma (14) found that removal of the acid amide groups in collagen decreases the fixation of formaldehyde in the pH region 2.0–3.5. Similar results were reported earlier by Wormel and Kaye (12) with casein. It is, therefore, quite likely that the reactivity of acid amide groups is increased in this pH range in the presence of salts like acetate and lactate. A flattening of the curve in the range pH 3.0–4.0 is also observed in the case of sodium lactate and magnesium acetate, probably indicating the completion of reaction with acid amide groups in this region. The cause for the relatively lower fixed formaldehyde in the pH range 3.5–5.0 in the presence of salt is not clear. However, in this pH region, swelling is greater in the presence of salts than in the control. The lyotropic effect of salts on swelling in this region might have an effect on formaldehyde fixation.

At pH 5.0 and above, the increase in fixed formaldehyde compared to control is expected. It is known (11) that the titration of a protein in the presence of salts (at constant anion concentration) markedly displaces the curves toward the basic side, and that at any given pH the number of basic groups discharged will be greater in the presence, than in the absence, of salts. With the increase in the available basic groups, an increase in the formaldehyde fixed is expected. This effect appears to be pronounced above pH 5.0 only.

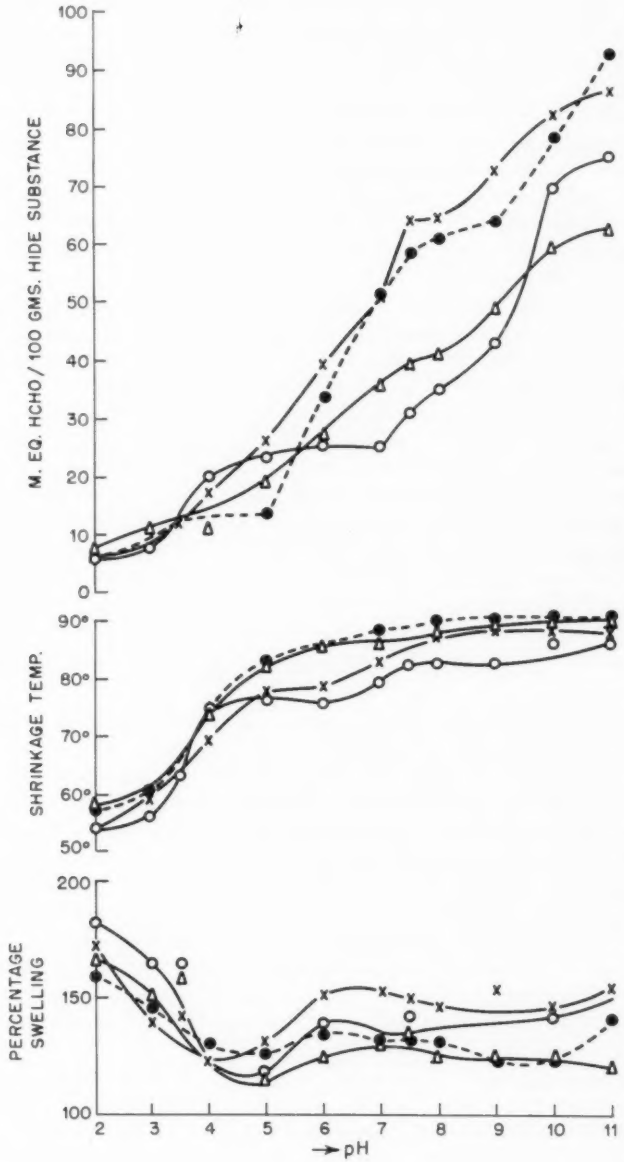

FIGURE 2.—Effect of pH value on formaldehyde fixation, shrink temperature, and swelling, when tanning in the presence of salts. ○—○—○ control (no salt); X—X—X Na acetate; △—△—△ Na lactate; ●—●—● Mg acetate.

The flattening of the curve at pH 7.0–8.0 is probably due to the completion of the reaction of basic amino groups of lysine with formaldehyde, and further increase in formaldehyde fixed above pH 8.0 is due to the guanidino groups of arginine coming into play.

Of the three salts under study, sodium acetate gave the highest values for fixed formaldehyde and sodium lactate the lowest. Magnesium acetate gives slightly lower values than sodium acetate, probably due to the cation effect. It was shown earlier that Na salts are better than Mg salts for increasing the fixation of formaldehyde. In the case of lactate, the formaldehyde fixed is increased only in the pH range 6–9.0, and this increase is also not very great compared to the control.

The presence of salts reduces the swelling at pH 2.0–4.0, increases swelling in the range 4.0–5.5, and decreases it at pH 6.0 and above, compared to the control, except in the case of sodium acetate. In the presence of this salt, swelling is greater than for the control at all pH values above 4.0.

Shrinkage temperature increases in all cases up to pH 8.0, with no further increase at higher pH values. This is true both in the presence and absence of salts. This confirms the postulate that fixation of formaldehyde by the guanidino group does not increase the shrink temperature. In the presence of salts, the shrink temperatures are higher than in the control series, except for sodium acetate at pH 4.0. In every case a steep rise in shrink temperature begins at pH 4.0; probably more cross-links are formed at and above this pH value.

SUMMARY AND CONCLUSIONS

A study has been made of the effect of a number of salts on fixation of formaldehyde, shrink temperature, and swelling of formaldehyde-tanned collagen. In general, formaldehyde fixation and shrink temperature are increased by the presence of salts, the nature of both cation and anion, as well as concentration, exerting specific effects. A few inorganic salts decrease the fixation.

At pH 7.0, salts of organic acids are in general more effective than inorganic salts; sodium salts are more effective than those of potassium, magnesium, calcium, and aluminum, in that order; chlorides are more effective than sulfates. Of the 20 salts studied, sodium and magnesium acetate stand out as most effective in increasing formaldehyde fixation, followed by sodium dichromate, lactate, and citrate.

With an increase in the concentration of the salt, the fixed formaldehyde and shrinkage temperature are increased.

In the presence of salts, the fixed formaldehyde and shrinkage temperature are increased in the pH region 2–3.5 and pH 5–10.0, and they are decreased in the pH range 3.5–5.0. The increase in the acid zone may be due to activation of the acid amide group reaction. The cause for the decrease in fixed formal-

dehyde and shrink temperature in the pH zone 3.5–5.0 is not clear, but in this region the swelling is greater in the presence of salts than in their absence.

The increase in fixation of formaldehyde by collagen in the presence of salts has been attributed to the increase in the number of basic groups discharged. More work is in progress to elucidate the mechanism of protein-salt reaction and its influence on the formaldehyde tanning.

ACKNOWLEDGMENT

Our thanks are due to the late Director, B. M. Das, for kind permission to publish these results.

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THIRTY YEARS AGO

(*From* JALCA, *May*, 1927)

Delegates appointed to the convention to be held at the Leathersellers' Hall, London, England, on May 3 – 5, for the purpose of considering the unification of analytical methods for tanning materials and leathers were Dr. L. Balderston (then President of ALCA), F. H. Small, and C. R. Oberfell.

Papers in this issue included "The Unhairing Action of Stannous Salts" by H. B. Merrill and "Why Does Inactivation and Removal of Basic Protein Groups Decrease the Fixation of Cationic Chromium?" by K. H. Gustavson.

The preliminary program for the Twenty-fourth Annual Meeting, to be held in Cincinnati, included three papers by Dr. George D. McLaughlin and his associates, an address on enzymes by Dr. K. George Falk, an address on colloid chemistry by Dr. Martin H. Fischer, and a "tanners' day", featuring talks of a historical nature by well-known tanners. The convention announcement also mentioned that the Brooklyn Dodgers would be playing the Cincinnati Reds during the convention period, and that the Latonia race track would be operating. [*Wonder if any conventioners made their expenses—or had to hitchhike home!*]

HEATS OF WETTING OF MODIFIED COLLAGEN AND OTHER MATERIALS

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ABSTRACT

The integral heats of wetting of modified collagens and other organic materials, including other proteins, plastics, and carbohydrates, were determined. Modifying collagen by treatment with acetic anhydride, methyl alcohol, or nitrous acid reduces the heat of wetting and the amount of moisture adsorbed under controlled conditions.

In general, materials that have a high percentage of hydrophylic groups give the highest heats of wetting. These hydrophylic groups include the free basic and acidic groups on side chains, hydroxyl groups, and nonhydrogen-bonded peptide groups. The heat of wetting is, however, also influenced by crystallinity and the physical state of the material. The basic and acidic groups of proteins attract water more strongly than the hydroxyl groups of carbohydrates. The determination of the heat of wetting offers a convenient procedure for measuring the hydrophilic properties of a material.

ABSTRACTO

Los calores integrales al mojar los colagenos modificados y otros materiales orgánicos, incluyendo otras proteínas, plásticos, y carbohidratos, fueron determinados. El modificar colagenos por el tratamiento con anídrido acético, metanol, o ácido nitroso reduce el calor del mojar y la cantidad de humedad adsorbida bajo condiciones controladas.

En general, materiales que tienen un alto porcentaje de grupos hidrófilos proporcionan los más altos calores. Estos grupos hidrófilos incluyen los grupos ácidos y básicos libres en cadenas laterales, grupos de oxidrilos, y grupos peptidos sin uniones de hidrógeno. Los calores al mojar son, sin embargo, también influenciados por la cristalinidad y el estado físico del material. Los grupos ácidos y básicos de proteínas atraen agua más fuertemente que los grupos de oxidrilos de los carbohidratos. La determinación del calor al mojar ofrece un procedimiento conveniente para medir las propiedades hidrófilas del material.

INTRODUCTION

A recent study (1) has shown that collagen, leather, and other organic and fibrous materials give off heat when they are placed in an excess of water. The amount of heat given off depends upon the type of material and the amount of moisture it adsorbs. The lower the moisture adsorption of the material concerned, the less the amount of heat evolved on wetting. It was also shown that the amount of heat evolved by a dry material was related to the amount of moisture adsorbed at 65% relative humidity and that the magnitude of the heats of adsorption was comparable to that of the heats of wetting.

In consideration of the results of these investigations, it is apparent that the integral heat of wetting is a characteristic of a material that is related to its hydrophilic properties. The measurement of the heat of wetting provides a quick and simple procedure for obtaining an over-all estimate of these properties. Such a test might be useful for the measurement of the comfort of clothing and as an aid in the evaluation of materials to be used for waterproof coatings.

Since it has been assumed that the adsorption of water takes place on the polar groups of a high polymer, the heat of wetting might be used to follow a reaction in which a polar group was modified by esterification or other chemical treatment. The results of the foregoing investigation also show that the test may be used for following other changes that occur in material of high molecular weight, such as aging and changes in state.

In the present investigation, determinations of the integral heats of wetting were made on collagen modified by deaminization, acetylation, and methylation, and on other organic and fibrous materials differing in structure and in hydrophilic characteristics. The relation between the heats of wetting and the polar groups in the molecule is discussed.

PREPARATION OF MATERIALS

A purified grade of collagen was used in preparing deaminated, methylated, and acetylated collagen derivatives. The source of collagen was a steer hide obtained within an hour after the death of the animal. The grain and flesh layers of the hide were split off, after which the corium (center split) was ground to a powder and freed of extraneous fats, salt, and proteins by a series of aqueous and organic extractions. The final product was ground in a Wiley mill to pass a 4-mm. sieve.

The method of Thomas and Foster (2) as modified by Bowes and Kenten (3) was used to deaminate the collagen powder. For samples deaminated one hour or less the following procedure was used: Collagen (150 g.) was soaked overnight in a liter of distilled water. The beaker containing the collagen-water mixture was placed in a water bath at 16° C. Sodium nitrite (150 g.)

was dissolved in the mixture, after which 150 ml. of glacial acetic acid was added. The reaction mixture was stirred continuously throughout the first hour. At selected intervals a portion of the contents of the reaction vessel was removed and transferred to a sintered glass funnel. The product was thoroughly washed with water, and, after being dehydrated with several alcohol and acetone extractions, was allowed to dry at room temperature.

The procedure for samples deaminated longer than one hour differed only in that CO_2 was bubbled through the reaction vessel to minimize oxidation of nitrous acid to nitric acid and to provide a means of continuous agitation. For each day the reaction was allowed to proceed, a fresh portion of the deaminating solution composed of the same amounts of nitrite and acetic acid as originally used was added.

The color of the deaminated derivatives ranged from yellow for that reacted for as much as 30 minutes through a straw-brown to a reddish brown for that reacted for two days.

The amino nitrogen content of the deaminated samples was obtained from quantitative determinations of the lysine and hydroxylysine contents of these derivatives made by a paper chromatographic procedure (4).

The methylated collagen derivatives were prepared according to the procedure of Fraenkel-Conrat and Olcott (5), as modified by Gustavson (6). Collagen was dehydrated with acetone, after which the acetone was removed at reduced pressure. Twenty-gram portions of the dry collagen were reacted from two hours to four days at 25° C. in two liters of absolute (dehydrated) methonol which was 0.1 *N* with respect to hydrochloric acid. The methylating mixtures were transferred to a water bath (temperature 1° C.) and sufficient sodium hydroxide solution to neutralize the hydrochloric acid was added in drops with constant stirring. The neutralized solutions were removed by filtration. The methylated products were washed several times with 50% aqueous alcohol, water, and finally acetone, and were dried at room temperature. The methoxyl contents of the methylated derivatives were determined by the microanalytical Zeisel method proposed by Steyermark (7).

Collagen was acetylated according to the procedure suggested by Green and coworkers (8). Dehydrated collagen was reacted with a 5% solution of acetic anhydride in glacial acetic acid for periods of one to eight hours at 25° C. This procedure restricts the acetylation primarily to the amino groups of the protein. The acetylated collagen derivatives were extracted with acetone in a Soxhlet extractor for 48 hours to remove uncombined reactants, and were dried at room temperature. The acetyl contents of the acetylated derivatives were determined by acid hydrolysis, followed by steam distillation and titration (8).

All the synthetic fibers and the silk, wool, cotton, and rayon were extracted with chloroform before determinations of heats of wetting were made. All other materials were commercial grade and were used as received.

Determinations of the heats of wetting were made as described by Kanagy (1) after drying the specimens for 24 hours at 100° C. Measurements of water adsorbed at 25° C. at relative humidities up to 75% were made as described by Kanagy (9).

RESULTS AND DISCUSSION

The effect of deamination on the heats of wetting of collagen is shown in Table I and Fig. 1. These results show that with a decrease in the lysine

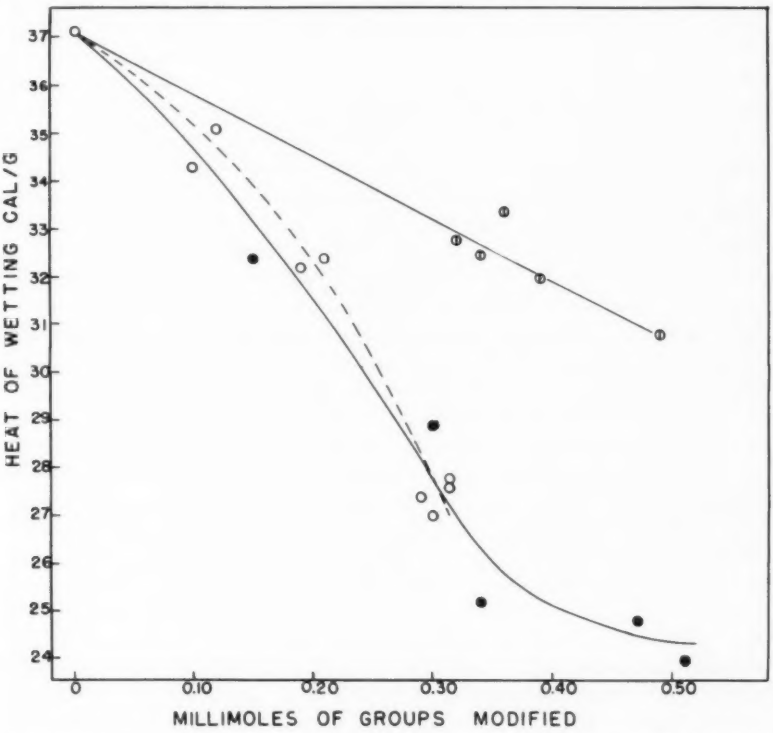

FIGURE 1.—Effect of deamination, methylation, and acetylation on heat of wetting of collagen.

○ Deaminated collagen
● Methylated collagen
Acetylated collagen

and hydroxylysine amino nitrogen, the heat of wetting is reduced. The decrease in the heat of wetting with the deamination treatment indicates that the introduction of an OH group in place of an NH_2 group renders the collagen less hydrophilic.

TABLE I

EFFECT OF DEAMINATION ON THE HEATS OF WETTING OF COLLAGEN

Time of Treatment	Millimoles Amino N per g. Collagen*	Heat of Wetting cal/g
0	0.335	37.1
5 min.	0.240	34.3
15 min.	0.219	35.1
30 min.	0.144	32.2
1 hr.	0.123	32.4
4 hr.	0.041	27.4
12 hr.	0.034	27.0
23 hr.	0.034	26.0
32 hr.	0.020	27.6
50 hr.	0.020	27.8

*Calculated from lysine plus hydroxylysine content.

TABLE II

WATER ADSORPTION OF DEAMINATED COLLAGEN DERIVATIVES

Material	% Water Adsorbed					
	Relative Humidity, %					
	6.0	11.1	22.0	32.5	56.0	75.0
Collagen	4.6	6.7	9.8	12.5	19.1	27.1
Collagen, deaminated 30 min.	4.3	6.2	9.2	11.9	18.9	26.3
Collagen, deaminated 4 hr.	4.2	5.8	9.5	12.0		

TABLE III

EFFECT OF METHYLATION ON THE HEATS OF WETTING OF COLLAGEN

Time of Treatment	Millimole Methoxyl per g. Collagen	Heat of Wetting cal/g
0	0	37.1
2 hr.	0.15	32.4
5 hr.	0.30	28.9
1½ days	0.34	25.2
3 days	0.51	24.0
4 days	0.47	24.8

The results for the water adsorption of the deaminated collagen derivatives at various humidities are shown in Table II. The water adsorption is decreased by deamination; this result is in line with the measurements of the heat of wetting.

The results of the measurements of the heats of wetting on collagen after methylation are reported in Table III and Fig. 1. Although the number of millimoles of methoxyl reacting per gram of collagen is equivalent to only about one half of the available carboxyl, the heat of wetting is reduced to slightly less than two-thirds of its original value. The further decrease in the heat of wetting after the addition of about 0.34 millimoles of methoxyl is, however, slight.

Water adsorbed by the methylated samples is shown in Table IV. No significant difference is observed between the samples methylated 1½ days (0.34 millimoles methoxyl) and 3 days (0.51 millimoles methoxyl). This is in accord with the data on heat of wetting for these two samples. The water adsorption of the sample containing 0.15 millimoles of methoxyl (methylated 2 hours) is the same as that of the sample in which 0.19 millimoles of amino groups (Table I, 30-minute deamination) have been destroyed; the same effect is also shown by the data on heat of wetting.

The effect of acetylation on the heat of wetting is shown in Table V and Fig. 1. Under the conditions employed in this experiment, the acetylation is shown to occur primarily on the amino group. The results show that by the combination of 0.49 millimoles of acetyl, which is more than equivalent to the amino nitrogen content, the heat of wetting is reduced from 37.1 to 30.8 calories per gram. This indicates that the introduction of the acetyl group reduces the hydrophilic properties of the amino group.

The water adsorption of acetylated collagen derivatives is shown in Table VI. After 8 hours of acetylation the water adsorption is reduced more than for either the deaminated or the methylated derivatives. The reduction in water adsorption after acetylation for one hour is at least 50% of the reduction after 8 hours of acetylation.

The heats of wetting of typical carbohydrates and proteins are shown in Table VII. Of the carbohydrates examined, starch and viscose rayon had the highest heats of wetting. The starch, a water-soluble form, has a highly branched structure, with the result that its many terminal OH groups contribute hydrophilic character to the material. The effect of crystallinity on the heats of wetting is shown by comparing cotton with the two materials just mentioned. Cotton is highly crystalline and consequently its reactive groups are not all available to water. On the other hand, the regeneration process employed in the production of viscose rayon evidently exposes water–adsorbing groups. Cellulose acetate rayon and the two ethyl celluloses demonstrate the effect of substitution of the active hydroxyl groups on the heat of wetting.

TABLE IV

WATER ADSORPTION OF METHYLATED COLLAGEN DERIVATIVES

Material	% Water Adsorbed					
	Relative Humidity, %					
	6.0	11.1	22.0	32.5	56.0	75.0
Collagen	4.6	6.7	9.8	12.5	19.1	27.1
Collagen, methylated 2 hr.	4.4	6.3	9.5	12.1	19.2	26.7
Collagen, methylated 1½ days	4.2	5.9	8.7	10.9	16.7	23.4
Collagen, methylated 3 days	4.0	6.0	8.8	11.3		

TABLE V

EFFECT OF ACETYLATION ON THE HEATS OF WETTING OF COLLAGEN

Time of Treatment	Millimoles Acetyl per g. Collagen	Heat of Wetting cal/g
0	0	37.1
1 hr.	0.32	32.8
2 hr.	0.34	32.5
3 hr.	0.36	33.4
5 hr.	0.39	32.0
8 hr.	0.49	30.8

TABLE VI

WATER ADSORPTION OF ACETYLATED COLLAGEN DERIVATIVES

Material	% Water Adsorbed					
	Relative Humidity, %					
	6.0	11.1	22.0	32.5	56.0	75.0
Collagen	4.6	6.7	9.8	12.5	18.5	26.4
Collagen, acetylated 1 hr.	4.1	6.0	8.7	10.9	16.7	23.0
Collagen, acetylated 8 hr.	4.0	5.1	7.7	9.9	15.5	21.8

The results for the proteins show that collagen has a much higher heat of wetting than any of the others. The high heat-of-wetting value for collagen is the result of several contributing factors. Because of its high proline and hydroxyproline content, the polypeptide chains are not so rapidly compact-

ed into a highly crystalline structure but are rather loosely grouped to form amorphous regions, the latter being very accessible to water. Reference to Table VIII shows that wool, blood albumin, and casein each have a higher polar amino acid content than collagen. In addition, the presence of phosphoric acid groups adds to the polar group content of casein. However, the heat of wetting of collagen is more than twice that of zein and egg albumin, and slightly less than twice that of wool or casein.

TABLE VII

HEATS OF WETTING OF TYPICAL CARBOHYDRATES AND PROTEINS

	Heat of Wetting cal/g.
Carbohydrates	
Starch	21.8
Viscose rayon	21.4
Cotton	11.2
Cellulose acetate rayon	8.6
Ethyl cellulose — 43.5% ethoxy	6.4
Ethyl cellulose — 52.0% ethoxy	3.0
Proteins	
Collagen	37.1
Wool	20.8
Casein	19.2
Zein	16.6
Blood albumin	16.1
Egg albumin	13.7
Silk	13.7

TABLE VIII

MOLES OF POLAR ACTIVE GROUPS IN 10^5 GRAMS OF DIFFERENT PROTEINS

Proteins	Polar Active Groups		Peptide Group	Total Polar Groups Including Peptide Group
	Based on Amino Acid Analysis without Any Correction	Based on Method of Pauling, Adjusting for Proline and Hydroxyproline		
Collagen	386	622	1105	1491
Casein	441	539	852	1293
Wool	458	528	934	1392
Blood albumin	443	487	851	1294
Zein	361	453	909	1270
Egg albumin	362	393	855	1217
Silk	287	294	1307	1594

TABLE IX

HEATS OF WETTING OF TYPICAL SYNTHETIC FIBERS AND SYNTHETIC PLASTICS

	Composition	Heat of Wetting cal/g
Synthetic Fibers		
Vicara	Zein	17.3
Nylon	Polyamide	6.6
Acrilan	Vinyl acetate-acrylonitrile	1.5
Dacron	Polyester	1.0
Dynel	Vinyl chloride-acrylonitrile	0.7
Orlon	Polyacrylonitrile	0.6
Glass fiber	Glass	0.5
Plastics		
Polyvinyl alcohol		9.4
Polyethylene		0.6
Polymethylmethacrylate		0.2
Polystyrene		0.06
Polyvinyl chloride		0.05

TABLE X

EFFECT OF DEGRADATION ON HEATS OF WETTING

NYLON FILMS

Number as Designated in RP 2210	Heat of Wetting: Not Exposed to Light cal/g	Heat of Wetting: Exposed to Light cal/g
4407	4.4	3.8
4410	3.2	2.6
4406	3.7	3.7
4408	3.7	3.1

COLLAGEN
(*Heated in oven*)

Heating Conditions: Time Days	Heating Conditions: Temperature °C	Loss in Weight* %	Heat of Wetting cal/g
1	100	13.33	37.1
7	100	14.69	35.8
7	120	15.60	32.4
7	140	16.66	26.8
7	160	20.55	20.1

*Includes water adsorbed under standard conditions.

The active hydrophilic groups in wool are similar in type and amount to those in collagen with the exception of the hydroxyproline OH group. Wool is, however, a highly crystalline protein; this probably has an influence on its ability to absorb water. The heat of wetting of silk is lower than that of any of the other proteins tested. This is probably because it is highly crystalline and contains a very low percentage of the basic and acidic amino acids.

Pauling (10) has assumed that, for every proline and hydroxyproline residue, a peptide carbonyl is free to form hydrogen bonds with water rather than with the imino group of the opposite polypeptide chain. The data of column 2 of Table VIII were obtained by Pauling's method and the correlation with heats of wetting (Table VII) is very good. Wool and casein, and blood albumin and zein, are slightly out of line, but in general the agreement is good. The inclusion of the peptide group as an active polar group gives a much poorer correlation. Silk especially is far out of line if the peptide group is included, and for this highly crystalline protein probably no water is adsorbed at the peptide linkage.

Heats of wetting of typical synthetic fibers and synthetic plastics are given in Table IX. Vicara, the fiber made from zein, is the only fiber that gives an appreciably large heat of wetting. The figure of 17.1 calories per gram for Vicara agrees closely with the value of 16.6 which was obtained for zein. Low values are obtained for the other fibers except nylon. The only appreciable heat of wetting for the plastics is the one for polyvinyl alcohol.

The effects of degradation on the heats of wetting are given in Table X. Some nylon films that had been exposed to ultraviolet light were compared to similar films that had not been exposed. The description of these films is given in NBS Research Paper No. 2210 (11). Exposure to light lowered the heat-of-wetting value for three of the four films.

Samples of collagen were heated in an oven at different temperatures, and heats of wetting were determined on the dry specimens. The results show that collagen loses additional weight as the time and temperature of heating are increased, and that the heat of wetting is decreased almost 50% by heating the material at 160° C. for 7 days.

The effect of degradation on heats of wetting can be explained by the fact that degraded materials contain more compensated hydrogen bonds. If the hydrogen bonds are internally compensated, the material is unable to absorb moisture instantaneously and give a characteristic heat of wetting.

The effect of the physical state of a material on its heat of wetting is shown in Table XI. Two examples are given. In the first example untreated collagen is compared with water—shrunken collagen and with gelatin, which is an amorphous type of collagen. The heats of wetting for both shrunken collagen and gelatin are lower than that of the original collagen. The shrinkage reaction apparently involves the internal compensation of hydrogen

bonds, and consequently less heat is evolved when shrunken collagen or gelatin is wetted.

TABLE XI

EFFECT OF CHANGE IN PHYSICAL STATE ON THE HEATS OF WETTING

	Heat of Wetting cal/g
Protein	
Collagen	37.1
Shrunken collagen	27.6
Commercial gelatin	25.6
Carbohydrates	
Cotton	11.2
Viscose rayon	21.4

The second example portrays an effect which is the opposite of the first. On treatment with chemicals used in the preparation of viscose rayon, highly crystalline cotton cellulose is converted to a material of very low crystallinity. Active groups become accessible to water during this process, and as a result more heat is evolved on wetting the viscose. This is shown in Table XI where viscose rayon is compared with cotton.

From the data of Table VII for the carbohydrates, an indication of the activity of the OH group of cellulose toward the adsorption of water can be obtained. A content of 43.5% ethoxyl groups in ethyl cellulose is equivalent to substitution of slightly more than 2 OH groups per glucose unit. The heat of wetting should, therefore, be reduced by two-thirds if each of the OH groups is equally active. The value of 6.4 calories per gram given in the table for 43.5% ethoxyl ethyl cellulose is only slightly less than one-third of the value obtained for viscose rayon.

Rowen and Blaine (12) give data to show that the adsorption of water vapor by viscose rayon at 96.8% relative humidity is 14.5 millimoles per gram. On the basis of 10^5 grams this value is 1450 moles. This weight of cellulose contains 1850 moles of hydroxyl, and therefore the weight of water adsorbed is slightly less than 1 mole per mole of hydroxyl. Values for the water adsorption of wool and silk obtained under the same conditions as those obtained for viscose rayon by Rowen and Blaine are 1440 and 1150 moles per 10^5 grams of material, respectively. From the number of polar-active groups for wool and silk given in Table VIII, it may be assumed that possibly 3 moles of water combine with each polar group. It therefore appears that the polar groups in the protein are more active in adsorbing water than the hydroxyl group in cellulose.

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. . . The nation's manpower needs in general and education's needs for teachers require notable expansion of the nation's facilities in higher education. In the extension of higher education, reforms and developments in program may be and should be undertaken . . . But whatever the developments and whatever the possibilities for improvement in higher education may be, the basic fact of the need of larger numbers of people with more higher education is incontrovertible . . .

Since 1950 the proportion of the very able who continue their education beyond high school has increased markedly but the wastage in this area is still distressing. A fuller cultivation of the talents of the able high-school seniors would add to the quality of their lives, and would provide additions of trained manpower for long periods of service in areas where training and experience are needed. Of the half of the top quarter who did not go beyond high school in 1950, roughly half were deterred by economic reasons, and the others were deterred by lack of motivation or interest or objective.

—*Manpower and Education*. Washington, D. C.: Educational Policies Commission, National Education Association, 1956.

. . . If we add up all of the apparently reasonable and carefully made estimates of manpower demands for the next five or ten or fifteen years, we arrive at a total that is greater than any reasonable expectation of what the colleges and universities will produce . . . The basic fact is that the total pool of young men and women reaching the age of entering the labor force is smaller than the total demand; moreover, the total number graduating from college is smaller than the number of openings for people with college training.

Since the educational system will not be able to satisfy the nation's entire appetite, it has the task of making as good use as possible of the resources we do have. In this situation we must pay attention to the quality as well as to the numbers of manpower trained for each of the professions. For the last several years we have been talking about the many able high school graduates who, for one reason or another—either motivation deficit or money deficit—do not now go to college. To the extent that we can get these students into college, we can do a better job of fulfilling the nation's manpower demands.

—Dael Wolfle, American Association for the Advancement of Science, in *The Strength to Meet Our National Need*. Washington, D. C.: American Council on Education, 1956.

THE EVALUATION OF TANNERY WASTES

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ABSTRACT

Before deciding on any method or process for treating tannery wastes, a survey must be conducted to determine the amount and characteristics of the total effluent and of the portions of the effluent originating in each tannery operation. Of equal importance is a survey of the receiving stream to determine the effect of the effluent on the stream, since the amount and character of treatment required are determined by the difference between the total pollutional potential of the effluent and that which the receiving stream can tolerate without impairment of its over-all value to the community. Methods for conducting such a survey are described.

ABSTRACTO

Antes de decidirs por algún método o proceso para tratar los desperdicios de una tenería, un estudio debe ser conducido para determinar la cantidad y las características del efluente y de las porciones del efluente originadas en cada operación en la tenería. De igual importancia es un estudio de la corriente que recibe el efluente para determinar el efecto del efluente en la corriente, ya que la cantidad y la clase del tratamiento requeridas son determinadas por medio de la diferencia entre la corrupción potencial total del efluente y esa que la corriente que lo recibe puede tolerar sin deterioro en el valor total a la comunidad. Métodos para conducir un estudio semejante son descritos.

Large quantities of water are required for the conversion of hide substance into leather. This water serves as the medium in which the various "wet work" operations are conducted; it functions as a carrier of, and a solvent for, the reagents necessary for the conversion, and it acts as a reagent in its own right. During the various operations, the process waters leach out, or otherwise remove, considerable amounts of soluble and insoluble matter from the hide. These water-borne leachates and unconsumed reagents constitute

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the waste effluents from the tannery. As a whole, these effluents are characterized by large volume, high color, and high content of dissolved and suspended matter both organic and inorganic. In some instances, the combined effluent may contain pathogenic microorganisms or significant amounts of toxic compounds. It has often been pointed out that, although tannery effluents may not be as readily putrescible as those from certain other industries, their effect on the receiving stream may, nevertheless, be extremely damaging. Large quantities of suspended solids will, under the usual stream conditions, settle out to form extensive sludge beds. The hexavalent chromium compounds in some chrome tannery effluents not only prevent the actual determination of the pollutional potential of the effluent but also have a direct toxic action on the microbiota and other organisms in the receiving stream.

The ever growing necessity for the conservation of our water resources dictates that the discharge of these voluminous and intractable wastes shall inflict no damage on the receiving stream which is inconsistent with its maximum utilization by all who are entitled to its use. To meet this requirement, local, state, and regional regulatory bodies have been set up, and minimum standards promulgated. The tanner, both as a citizen and user of water and streams, is faced with the problem of treating and disposing of his plant effluents in compliance with the requirements of these bodies and the dictates of sound public health and conservation practice. He may accomplish this end by one or more of the following procedures:

1. Reuse of one or more of his process effluents.

2. Discharge into a municipal sewerage system with or without prior treatment.

3. Disposal by dilution, into a nearby body of water.

4. Treatment, in varying degree, of the effluent. This may be merely a primary treatment, involving more or less complete removal of the settleable solids, with or without precipitation of dissolved or suspended matter. The sludge thus removed may be buried, burned, or otherwise disposed of. The supernatant from the primary treatment may be discharged directly into a municipal sewer or a nearby body of water, or may receive a secondary treatment to further reduce its pollutional potential.

The first alternative should always be considered, regardless of the subsequent treatment of the effluent. Its successful utilization will result in lower over-all water costs and a reduction of the volume of wastes to be treated. The second alternative is practicable only when the tannery is located in an urban area with sewage treatment facilities adequate to handle the additional load contributed by the tannery, or where the tannery is willing to bear its share of the cost of building, operating, and maintaining cooperative facilities capable of treating its own wastes plus those of the community. The

third alternative is, at this time, practically nonexistent. There are few, if any, watercourses which can receive even intermittent discharges of tannery wastes without a serious effect on their use by industries or communities along their shores. The fourth alternative is the one to which the tanner will usually have to resort. Under certain conditions, some type of pretreatment will be necessary even if discharge into existing domestic or industrial waste treatment plants is possible.

The type and extent of treatment will depend upon many factors. Of necessity, the method of handling the plant's wastes will be the heart of the tannery's pollution abatement program. It should be flexible and readily adaptable to meet changes imposed by production schedules and requirements. It should meet the minimum requirements of all regulatory agencies concerned. It should be based on a careful consideration of the economics of the situation so that the costs of construction, operation, and maintenance will not be out of line with the tannery's ability to meet them. The scientific principles upon which the treatment is based should be valid in concept and operation. The operation and control of the process should be as simple as possible, consistent with the effective treatment of the wastes. Last but not least, the design and construction of the physical plant and its appurtenances should be based on sound engineering principles. The extent to which these conditions are met will determine the cost and effectiveness of the tannery's wastes disposal program. In order to expedite and integrate the planning and preparatory phases of the program, the project should be placed under the direction of a technically qualified person.

Before a waste can be treated effectively, it is essential that certain information about it and the stream into which it will eventually be discharged be known. The choice of treatment procedures and the design of treatment facilities must be based on the proper evaluation of reliable data derived from a carefully planned and well executed survey. This survey should provide sufficient data so that the action recommended will take cognizance of future as well as present needs of all groups who make use of the waterway. To accomplish this, three types of information will be required: (1) that obtained by observation, measurement, sampling, and laboratory analysis; (2) that obtained from governmental, civic, and regulatory groups; and (3) that obtained by extrapolation from the data obtained in (1) and (2).

At least four factors must be considered in the selection and evaluation of the categories of information just noted. These are:

1. The present over-all use of water by the plant and in the separate operations carried out therein; the minimum water requirements for the whole plant and for each of the separate operations; the amount of water that may be needed within the forseeable future for expanded operation; physical and chemical characteristics of the water required for each tannery operation.

2. The chemical, biochemical, physical, toxicological, and microbiological characteristics of the individual process effluents and of the combined wastes.

3. The chemical, physical, microbiological, and macrobiological characteristics of the receiving stream.

4. The present and contemplated uses of the stream as well as the various regulations governing the discharge of effluents into its waters.

As a result of our experience in the evaluation and surveying of industrial wastes, we have developed a procedure for the analysis of waste disposal problems in terms of these factors.

Liquid-borne wastes are, essentially, dilute dispersions of dissolved and suspended matter. In order to evaluate the extent of the treatment or disposal problem, it is essential that an accurate picture of the tannery's water requirements be known. The first step, therefore, concerns itself with this aspect of the problem. Four major groups of data are determined at this point: (1) water quality requirements, (2) total and individual process water requirements, (3) actual volumes of water used (total and individual processes), and (4) the tannery's "water balance".

Each tannery should set up standards of quality, clearly indicating the optimum chemical, physical, and biological characteristics of the waters needed in the various processes and other operations. The establishment of such standards is the first step toward real water economy. Properly used, they will indicate the degree of treatment required to make any supply useable. They will also make possible an intelligent choice between two or more supplies or indicate whether a process effluent may be safely reused.

An estimate of the tannery's present water use should be made. This information should be supplied by the heads of all departments that use water and should be based on an honest appraisal, without recourse to measurements of any kind. Data regarding optimal volumes of water required for steam production, cleaning, and subsidiary operations should be obtained from all personnel concerned, from the experience of other tanners, and from scientific studies where available. Each department's estimate of present use should be compared with the "ideal" volume required. This portion of the study serves two purposes. It gives management an idea regarding water requirements under similar conditions and supplies a picture of the staff's thinking on the question of water use.

The water streams entering the plant and each individual department are then gaged and metered to determine the *actual* amounts of water used in the tannery and in each operation. This information is then compared with the estimates previously submitted, with data from similar operations, and with "ideal" estimates. The amount of water lost through spillage and leakage is determined.

At this point an inventory of water use within the plant is available: the desired quality of the process waters and their actual characteristics; the volumes of water used and the optimal quantities needed for each operation; and the quantities of water wasted. The latter data are derived from the difference between the water actually used and the amount required. A "water balance" can now be made for the tannery. If there is no difference between the water actually used and the required amounts, the plant is in water balance. If the plant uses less water than the estimated requirements, the plant is in positive water balance. Usually, actual requirements will be significantly less than the amount of water measured as it enters the tannery. Under this condition, the plant is in negative balance. The difference represents the wastage which can be eliminated by a program of water conservation. Often, it represents a significant portion of the entire plant effluent. The volume of water entering the plant represents, to all intents and purposes, the volume of wastes which will have to be treated. A tannery in negative water balance is not only wasting water; it is adding to the cost of its wastes treatment program.

Two considerations should be noted in connection with water wastage. First, it is usually preferable to treat concentrated wastes rather than overly dilute effluents. Secondly, the volume of waste to be treated materially affects the size and type of plant required for its treatment. It goes without saying that the cost of a treatment plant is related to its size. It can thus be easily seen that water conservation lowers processing costs as well as charges for wastes treatment.

The second step in the survey concerns itself with the waste and its components. The total tannery effluent is determined by metering. In addition, the volume of waste contributed by each process or operation is determined under various production conditions. Where this is impracticable, maximum and minimum volume should be extrapolated from obtainable data. Whether or not these volumes can be reduced will depend upon data obtained in the previous portion of the survey and from laboratory data which will be developed during the remainder of the study.

The laboratory aspects of the evaluation of the waste must be carefully planned. Samples must be so scheduled that maximum information can be derived from them. The samples must be representative, and a sufficient number of replicates must be taken to insure that the derived information will be valid statistically and will reflect the tannery's output. The analytical procedures are designed to provide the following information regarding the total effluent and its component streams:

1. *Physical Characteristics:* color, odor, temperature, total solids, settleable solids, suspended solids, dissolved solids, organic solids.

2. *Chemical and Biochemical Characteristics:* pH, biochemical oxygen demand, oxygen consumed, acidity, alkalinity, acidic and alkaline com-

pounds, reducing and oxidizing agents, toxic compounds, oils, greases, solvents, heavy metals, unusual compounds associated with specific processing operations.

3. *Biological Characteristics:* these are determined only when indicated and may include pathogenic organisms, total counts, characteristic organisms, etc. Bioassays to determine the toxicity of an effluent to fish, plants, aquatic life, or livestock may be necessary in certain instances.

It may be pertinent, at this point, to say a few words regarding the significance of some of these determinations. The solids dispersed in a waste effluent are divided, for convenience' sake, into coarse and floating, settleable, suspended, and dissolved solids. Each of these may be either organic or inorganic, or both. Though some of these divisions are arbitrary, they are useful in the interpretation of field and laboratory observations.

Coarse and floating solids are obviously objectionable. They detract from the appearance of any body of water into which they find entry. In sufficiently large amounts, they may interfere with the use of the stream for navigational, recreational, and other purposes. From a technical point of view, they are troublesome in sewers, treatment plants, and streams. These solids may clog sewers and pumping equipment in the sewerage system or the treatment plant. In the stream, they have two major deleterious effects. When present in quantities sufficient to cover large portions of the water surface, they interfere with the stream's ability to reoxygenate itself, by mechanical interference with the absorption of oxygen and by interference with the photosynthetic activities of the stream's plankton and aquatic plants. Secondly, these solids settle out to form sludge banks. Since in this respect they are similar to settleable solids, their effect will be discussed under that heading.

Settleable solids represent those materials in the effluent which will settle out within a reasonable time. This period, for analytical purposes, is taken as one hour. These solids are objectionable both in the sewerage system and in the receiving stream. When they settle out, they affect the hydraulics of the sewers and may materially reduce their capacity. In the treatment plant, they increase the load on sludge-moving equipment, settling tanks, filters, digesters, and sludge-drying facilities. In the stream, they render the water turbid. This turbidity may be sufficient to cut down materially the penetration of sunlight into the water, reducing the photosynthetic activities of plankton and aquatic vegetation. This, in turn, diminishes the stream's ability to replenish its supply of dissolved oxygen. Plankton and aquatic plants are reduced in numbers since their capacity to synthesize nutrients has been decreased. This affects those organisms dependent upon them for food. The end result is that the ecologic balance of the waterway has been adversely affected.

Settleable solids, under usual stream conditions, may settle out to form sludge beds. As a result of the decomposition of their organic fraction, anaerobic conditions are soon established. The anaerobic degradation of these deposits results in the liberation of odors and gases which may or may not be toxic. The gases may be produced in sufficient quantity to disturb the mass of fermenting sludge and float portions into the body of the stream. Since these materials are organic, they impose an additional load on the available dissolved oxygen of the stream. The dispersed or redispersed solids may, mechanically, clog the gills of fish or kill small organisms upon which the fish feed. The resultant turbidity, when sufficiently high, represents many difficulties when such waters are to be treated for municipal purposes. Deposits of silt and sludge reduce the volumetric capacity of stream beds, lakes, and reservoirs. This may adversely affect water storage for municipal supplies, flood control, or power generation.

Suspended solids represent those solids which will not settle out within one hour. Often, they may be quite fine and resist settling for extended periods. However, given sufficient time and quiescent conditions, even fine solids will settle out. When present in sufficient amounts, they present a real problem. Their effect on photosynthetic activity and reoxygenation are essentially the same as in the case of settleable solids. When present in amounts sufficient to give high turbidities, they affect municipal water treatment unfavorably. They may settle out to form deposits on the bed of the stream and there undergo anaerobic decomposition, or kill eggs and organisms required by fish or other biota of the stream. Since they present a larger surface area than either coarse or settleable solids, they deplete the dissolved oxygen of the water much more rapidly than the former.

The significance of organic matter has been included in the discussion of the various types of solids. Such matter is significant to the extent that it undergoes degradation. This degradation requires oxygen and thus represents a drain on the waterway's dissolved oxygen and its capacity to reoxygenate itself. When the supply of oxygen is depleted, anaerobic conditions are set up and the stream rapidly degenerates.

The temperature of tannery wastes is unimportant. The significance of odors is self-evident. Color is of real importance: not only are spent tans highly colored, they may react with iron compounds in the stream to form unsightly and intractable inks.

The dissolved solids in tannery effluents may represent putrescible organic materials or compounds which may react with other components of the plant effluent to form precipitates. In the case of chrome tanneries they include, among other things, chromium salts which inhibit the biochemical oxidation of the organic fractions in the waste or receiving stream. In addition, chromium compounds are directly toxic to the microbiota and fish of the stream. An extensive kill of either of these components of the waterway's economy

may prove disastrous. Sulfides are present, in appreciable quantities, in many tannery effluents. Depending upon pH, they may be present as H_2S or HS^- ions. Studies indicate that toxicity of sulfides increases with decreasing hydrogen ion concentration. However, both the undissociated gas and the ion are toxic to fish. The presence of the characteristic odor of H_2S is related to the acidity of the water carrier. Hydrogen sulfide, besides presenting an odor nuisance, is toxic to plant and animal life when present in sufficient concentration.

The effects of pH, acidity, and alkalinity will be considered together, since they are interrelated. pH and titrable acidity or basicity should not be confused. The former is a measure of the hydrogen ion concentration or "strength" of an acidic or alkaline solution. It is determined by the degree of dissociation of the acidic or alkaline compound and the solvent in which it is dissolved. Changes in pH value are influenced not only by the degree of ionization of an added acid or alkali but also by the solution's buffer capacity. The titrable acidity or basicity represents a solution's capacity to react with hydroxyl or hydronium ions, respectively. The acidity or alkalinity of a surface water represents its potential to neutralize basic or acidic effluents. This is rather limited because the buffering capacity of streams is relatively small. It is therefore important that a tannery effluent shall not overtax the receiving stream's ability to neutralize the acidic or basic compounds introduced with the waste.

Radical changes in the pH of a stream may affect its aquatic population adversely. The ability of the water's flora and fauna to tolerate changes in in pH is relatively limited. Although an acid or alkline effluent may inhibit or destroy only a limited portion of the stream's population, the remaining organism will be affected by resulting changes in their food supply or the waterway's ecologic balance. The differing degrees of tolerance of particular species, and the synergistic effects of compounds dispersed in the water, make it extremely difficult to give a pH range which is safe for the entire diversity of the biota in a body of water. In general, the pH should not be allowed to fall significantly below 6.0 or rise much above 8.0. Most fish, for instance, require a pH between 6.5 and 8.4. However, the type of acid, as well as pH and titrable acidity, plays a role.

Acid conditions may result in the liberation of toxic compounds such as hydrogen sulfide or hydrogen cyanide from dissolved salts. Effluents which depress the pH to low levels corrode metals and concrete in sewerage systems and treatment plants as well as boats and marine installations in the stream—to say nothing of their effect on vegetation. Low pH values have a sterilizing effect, reducing or inhibiting microbiotic activity, thus affecting the stream's ability to handle the waste itself.

Alkaline effluents may raise the pH or alkalinity of the water to undesirable levels. They may be directly toxic to aquatic life. They may react with

certain ions in the stream or other effluents to form precipitates. They may disperse suspended organic matter in the water with a consequent increase in color or biochemical oxygen demand. High bicarbonate alkalinity does not appear to be harmful to plankton or other aquatic life. However, there is evidence of an adverse effect on fish if the pH is raised much above 9.0. Of particular importance to tanners are studies indicating that calcium hydroxide is toxic to certain species of fish in concentrations as low as 18 parts per million.

Inorganic reducing agents, like organic matter, use up the dissolved oxygen of the receiving water. Their reaction with oxygen is almost immediate, in contrast to the much slower biological oxidation of organic compounds. The discharge of large quantities of sulfides or other reducing agents into a body of water constitutes a severe drain on its dissolved oxygen reserves. The end result is the depletion of the dissolved oxygen and the establishment of anaerobic or septic conditions. The presence of such materials in waters intended for municipal supplies complicates the treatment process. Since many tannery effluents are rich in sulfides, these effects are of particular concern to the tanner.

The biochemical oxygen demand (BOD) of a waste represents, in effect, its pollutional potential. There are technical objections to the procedures used in the determination and to the significance of the derived data. However, it is at present our best single criterion of the "strength "of a waste and the efficiency of a treatment process. By definition, BOD is the quantity of oxygen utilized in the biochemical oxidation of organic matter during a given period of time, under specified conditions, at a given temperature. Certain fractions of tannery wastes are characterized by a high biochemical oxygen demand. This simply means that they are highly pollutional and require large quantities of oxygen for their stabilization by biological procedures.

"Oxygen consumed" is another parameter of the pollutional potential of a waste. It represents the quantity of oxygen consumed by a given amount of waste when digested with an oxidizing agent such as permanganate or dichromate under standard conditions and is, therefore, the amount of oxygen required for the oxidation of a waste by chemical means. The data derived from this test cannot be compared directly with BOD measurements, since the reactions of biological metabolism are not the same as those involved in oxidation by strong reagents. However, it is a rapid test, occupying but a few hours as compared with days in the case of BOD determinations. It is particularly useful when evaluating strong wastes or effluents containing substances which inhibit biological activity—chrome wastes, for instance.

In the final analysis, the capacity of a receiving water to handle a waste is dependent upon its dissolved oxygen and its ability to reoxygenate itself. When an effluent depletes a stream's dissolved oxygen, anaerobic conditions

are initiated. Long stretches, or even the entire length of the waterway, may become a septic sewer. Fish and other aquatic life requiring oxygen will die out. The full use of the stream is impaired, and it may become a nuisance or a public health hazard. The importance of knowing the effect of an effluent on this parameter of stream sanitation can hardly be overestimated.

Certain fractions of tannery wastes may contain high concentrations of fats, greases, and oils. Besides being unsightly, these greases may be directly toxic to fish and other stream biota. They may coat the bodies of fish and birds and interfere with the metabolism of organisms which serve as their food. When present in quantities sufficient to cover large portions of the water, they may interfere with reoxygenation and photosynthetic activities. In the treatment plant they may interfere with the treatment of the waste.

Solvents present a hazard in the sewerage system, the treatment plant, and the stream. The inherent danger of flammable wastes needs no elaboration. In addition they may be deleterious to the biota of the stream, or otherwise interfere with treatment processes.

Heavy metals and chromium compounds are directly toxic to organisms living in the waterway. Even when present in quantities insufficient to produce extensive kills, they may inhibit the life activities of the water's populations or those of animals living along its shores. The inhibitory effect of hexavalent chromium on treatment processes is well known. Heavy metals may have a similar deleterious effect. Surface-active agents and other compounds associated with specific processing operations may complicate treatment procedures or have adverse effects on the stream.

The presence of pathogenic organisms in tannery wastes is rare in this country. Total counts and the determination of the types of organisms in a receiving water are valuable adjuncts in the study. However, unless funds are available and the project can be carried out cooperatively with other users of the stream, such studies are not indicated in a tannery's survey of a waterway.

It is oftentimes important to determine directly the effect of a waste effluent on the fish or other aquatic life of a stream, or on plants and animals using it or living along its shores. Although it is impossible at present to duplicate stream conditions in the laboratory, a bio-assay will give the tanner an idea of the effect of a waste on the plants or animals which will be exposed to it. A bio-assay is very valuable to a tanner when he is dealing with civic or regulatory bodies and will give him dramatic evidence regarding the biological effect of his effluents. It might be mentioned in passing, that the BOD test is a bio-assay. When bio-assays are impracticable for economic or other reasons, the literature should be searched for data regarding the biological effect of the toxic portions of a plant's effluent.

This short resume of the significance of some of the more important laboratory and field determinations performed on the receiving water and the

waste has been presented to give the tanner an idea of their practical importance. An evaluation of the data obtained from the laboratory studies will provide a basis for determining whether any of the waste effluents may be reused in the plant with little or no treatment, and which effluents should be segregated for economy and efficiency of treatment. Reduction of volumes of water used in processing and quantities of effluents may mean real savings in plant operation. Clear water pools offer a distinct possibility for reuse. These effluents represent about 35% of the total volume of waste but contain less than ½% of the substances having an oxygen demand. This portion of the survey will provide the tanner with an evaluation of the "strength" of the tannery's effluents and provide him with sound data for choosing an effective method of treating them.

The third step in the survey concerns itself with the receiving stream. This portion of the study resolves itself into three related divisions:

(1) the stream survey, (2) present and planned uses of the waterway, and (3) the effect of the wastes on the stream.

In considering the discharge of a waste into a body of water, it is essential that one take into account the probable effect of this discharge. This portion of the study should provide such information as:

(a) Stream flow, including seasonal variations and high and low flows of record.

(b) Stream ecology: types of plants and animals living within it or along its shores; animals depending upon it for food or water.

(c) Character of the receiving waters: (1) physical characteristics: color, temperature, types and quantities of solids dispersed therein; (2) chemical characteristics: dissolved oxygen, presence of ions or compounds capable of reacting with the waste to form precipitates or toxic compounds, other effluents now being discharged into it, alkalinity, acidity, etc.; and (3) classification of the stream: type of bottom, character of shoreline, types of industrial and municipal installations along its shores, present and contemplated uses of the waterway.

The significance of many of these determinations has been considered in the discussion of the evaluation of the tannery's effluent. The importance of the others is evident upon consideration of the potential of the stream to handle the wastes to be discharged.

The next portion of the task is done in close cooperation with regulatory and civic groups. The tanner must consider the "total" use of the stream. He must realize that the right to full utilization by all concerned must be protected, and that a workable, fair balance must be struck between the ideal and practicable aspects of stream sanitation. Certainly, the stream must be so maintained that maximal beneficial use will be preserved. Intelligent cooperation with civic bodies and regulatory agencies has a definite public

relations value and creates good will. Management is often surprised at the assistance such groups will give freely. The knowledge by the community and the government that a tannery is sincerely interested in establishing an effective pollution abatement program always results in mutual good will and an understanding of each side's problems. The good will engendered often prevents the enactment of overly strict or unreasonable legislation. It represents an intangible, but nevertheless valuable, resource of management.

When all the information has been gathered and evaluated, the extent and type of treatment can be prescribed. In effect, the extent of treatment will represent the difference between the pollutional and deleterious properties of the waste and the amount of pollution the stream can accept without unduly affecting its usefulness.

The plan outlined above for collection of these data and their analysis constitutes a method for evaluating a tannery's waste. Though it will probably have to be modified to meet specific conditions, it provides a reasonable and effective guide for the conduct of a wastes survey. Such a survey, if properly carried out, will provide:

1. A clear picture of the properties of the waste and its constituent effluents.
2. Basic information for possible water reuse and conservation.
3. A clear picture of the receiving stream and its ability to handle the proposed discharge.
4. A basis for cooperation with other industries using the waterway and with the community.
5. Data for the intelligent choice of a treatment process and the determination of the required degree of treatment, and design data for the treatment plant or other disposal procedures.

In considering treatment procedures and design criteria, it should be remembered that it is preferable to treat a small volume of strong wastes rather than a large volume of dilute wastes. Handling large volumes of wastes calls for increased outlays for construction, operation, and maintenance.

The best place to treat a waste is usually at its source. In all cases, the tannery superintendent should ask himself:

1. Can any individual process be modified so that there will be no, or significantly less, waste effluent?
2. Is the effluent from each process being kept at a minimum?
3. Can any of the effluents be reused? If so, how?
4. Which wastes can or should be segregated, to decrease over-all costs of treatment?
5. What is the treatability of the effluent?

6. Which effluents may be combined to increase efficiency of treatment or decrease treatment costs?

The actual treatment of tannery effluents is a large subject and not properly a part of this presentation. This paper has set forth what we have found to be a reasonable and effective approach to the evaluation of tannery wastes. Throughout, one cardinal principle has been emphasized: viz., in order to properly treat a waste effluent, one must know not only the chemical, physical, and toxicological characteristics of the waste but also its probable effect on the stream into which it will finally flow. This calls for laboratory and field investigations by qualified personnel as well as close cooperation with regulatory groups and the community in which the tannery is located.

DISCUSSION

MR. J. F. WAGONER (Armour Leather Company): We are indeed indebted to Mr. Luckens for coming here today and presenting a most interesting and instructive paper. I am sure you all appreciate that he has pointed up the important aspects of this problem of waste treatment and has emphasized the proper approach to the problem. I think one thing should be borne in mind. While we can generalize on the treatment of waste, it must be remembered that each tannery presents an individual problem and therefore requires a very careful survey and competent consultation.

I was extremely glad to notice that Mr. Luckens mentioned one phase of waste treatment that is receiving considerable attention by all industries today. That is the reduction in the volume of waste through the reuse of process wastes. This, of course, is an internal problem. Enormous strides along this line have been reported in many cases, and it is one that should be given serious consideration by the tanner. Such an approach in the tannery requires not only the assistance of the technical staff in charge of waste treatment but also the full cooperation of the tanner. After all, a quality piece of leather is our prime objective; therefore, any process changes that are to be effected will require the full cooperation of all concerned. I think it therefore behooves us, of the technical side of the industry, to cooperate with, and in turn solicit the cooperation of, the tanners themselves. This point is of particular importance in those cases where the waste is being treated along with public sewage, as in most cases the cost is based on a metered volume of waste. Perhaps some of you have had some experiences along this line and would care to tell us about them. I am sure that if anyone has any particular questions, Mr. Luckens will be very glad to answer them.

DR. HOOVER: I am not an engineer, but I have, for the past seven years, been working half-time on the treatment of dairy waste. The same problem, I am sure, comes up there as in your field, in tannery waste. That is, when the engineer comes in to make a survey, such as Mr. Luckens spoke of, the

management lets it be known through the plant that they are now going to have a waste disposal survey and says: "Tighten up, boys." The survey is made. (I am speaking of the dairy industry and not the tannery, at the moment). Then the results of that survey are given back to the same engineer, or another firm, and a plant is designed. It goes in. Everybody in the dairy thinks: We have no more waste disposal problems, we have a treatment plant. And the least increase in waste, from the survey to the plant operation, that I have seen is fourfold. In every plant that I have seen, the dairy put out at least four times as much waste on the day the plant went into operation as on the day the survey was made. Then the engineer is in trouble. If he designed a plant four times as large as the survey indicated, he would be in trouble for overdesigning the plant.

You have to play fair with the sanitary engineer who is doing the work for you, and that is a very difficult thing. It actually gets into personnel and plant relations. But I am sure Mr. Luckens does not object to what I am saying. It is essential that you make an honest survey, and that is not done very often.

MR. LUCKENS: I quite agree with Dr. Hoover. I know of Dr. Hoover's work and also that of my good friend Dr. Porges who works with him on dairy wastes. I think Dr. Hoover is, essentially, conservative. It happens, not only in dairy plants but in every industry where air or water pollution may be a problem. By the time the survey begins, everyone in production has been alerted. Every department "tightens up." During the period of the study, waste flows are kept at a minimum at all costs. The outcome is a survey and report which do not reflect the true conditions at the plant. A process and treatment plant which results from such a less-than-candid approach to the problem, is, more often than not, inadequate.

The attitude and policy of top management toward the evaluation of a wastes problem should be made known to all personnel. Complete candor and cooperation among all concerned in the undertaking are essential if an effective solution is to be achieved. It must be remembered that the consultant and his staff have been retained to protect the best interests of the organization within the framework of existing governmental regulations, the nature of the waste, good engineering practice, and sound economics.

Supervisory people possess a fair share of the common human frailties. This is to be expected. No one would have it any other way. Too often, department heads are, consciously or unconsciously, suspicious of the motives behind a wastes survey. They are, justifiably or not, fearful that their operations may be implicated as sources of pollution. Supervisors seem to feel that should their departments or processes be found to be contributors to the over-all waste problem, it would necessarily reflect on their technical and administrative abilities. This attitude frequently results in their keeping pertinent data from the investigator. Only those who are in a position to set

organizational policy can quiet these unfounded fears and suspicions which can only result in an unrealistic report.

The findings of a well conducted, impartial survey will often be questioned because the data do not agree with preconceived notions regarding the type, strength, or quantity of effluent from a given process or department. Here, too, top management must insist on full cooperation and unbiased discussion of findings with those who issued the report and made recommendations.

MR. GEORGE W. COLLIN (Virginia Oak Tannery, Inc.): There are several ways of treating tannery waste, including chemical and mechanical treatments and treatment by sedimentation plants. My first question is: Which one of those three is the most economical and most efficient for a vegetable tannery? Question Number Two: Have you had any experience with digestion tanks using activated sludge for vegetable tannery wastes?

MR. LUCKENS: Your first question presents a rather large order. It cannot be answered without more information about your tannery, the waste itself, and the stream into which it is to be discharged. Every waste must be studied as an individual problem, not only in terms of its composition but also in terms of the receiving stream and the economics of the situation. What will work in one case will not work in another. In addition, one must not lose sight of governmental regulations. Under certain conditions, it may only be necessary to control the discharge of the waste into the receiving stream after preliminary settling; in others, coagulation or secondary treatment may be essential. It is difficult, if not impossible, to give you a specific answer under these circumstances. I would venture to say that waste flows in your tannery could be substantially reduced by practicing segregation and the judicious reuse of certain beamhouse effluents. Water conservation, segregation of waste flows, and a well conceived water-use policy will often go a long way in easing an industrial waste problem.

In answer to your second question, no one, to my knowledge, has done extensive work on the treatment of tannery wastes by activated sludge. We have done quite a bit of work on the treatment of highly refractory wastes by activated sludge as well as on biofilters. We have developed strains which will utilize phenols and many complex organic intermediates, as well as other substances which are not normally utilized by the biota in a trickling filter slime or activated floc. It may be said without fear of contradiction that there are organisms in nature which can be (or may be) acclimated to utilize any organic substrate. We all know that there are organisms which produce tannases. It would seem reasonable to expect that, with a fair amount of work, a strain of organisms could be acclimatized to utilize tanhouse effluents in their nutrition. This would mean that your vegetable tans could then be handled biologically. However, this approach means that you must be prepared to go into a research program. Although

the chances of success would appear to be good, no one can be sure of the outcome or the actual amount of time, effort, and funds required to bring the program to fruition.

Incidentally, such an approach often pays unexpected dividends. The work of Porges and Hoover on the treatment of dairy wastes brings this out very well. They discovered vitamin B_{12} in activated sludge. The use of this material as a source of the vitamin is now being explored for commercial exploitation and appears to have a bright future. Often, research pays off with unexpected results. To look for serendipity in all research is, of course, naive. But well planned research pays off in wastes treatment as in anything else.

Received February 23, 1957.

HOW TO GET MORE OUT OF A CONVENTION

(Excerpts from an article by H. T. Sharp, in Chemical Engineering, *September,* 1956, *pages 226–32. Reprinted by permission. The original paper will repay study.)*

Convention-going can be a waste of time or a source of new information, new ideas and new friends. A bit of planning makes the difference. . . . . Planning starts with a clear statement of why you are going. . . . . Key to making a convention pay off is the study you give to the program. . . . . Presence of people with interests similar to yours is the most important feature of a convention.

Papers will likely be printed, but discussion may not be, and the time lag between delivery and printing may be appreciable. . . . . Many engineers judge a session worth attending only if it will yield specific answers to a current problem, or holds a paper of basic importance revealing significant information for the first time, or promises an intensive and stimulating discussion period.

To a newcomer, getting to know people is something of a problem. . . . . One of the easiest ways is to start with the speakers. The subject the speaker covers is naturally good conversation fodder. He's apt to be quite willing to discuss it. Often it is best to try to see him later when he has a free moment (rather than just after the session when many would-be questioners are waiting to see him). . . . . But the best way to get acquainted is also the simplest,—just introduce yourself. Best times for making such contacts are at receptions and while waiting for sessions to begin.

When planning what you'll do at a convention, remember that old saw, "The mind cannot absorb what the fanny cannot endure."

You can boost the value of any meeting by jotting down a few notes on what you've learned there.

LIFE LINES

Brief Biographies of Our Contributors

J. M. CASSEL.—See the May, 1956, issue of *JALCA*.

K. S. JAYARAMAN received his bachelor's degree in leather technology from the University of Madras and has submitted his thesis for the master's degree. He has been associated with the Central Leather Research Institute since 1953.

J. R. KANAGY.—See the March, 1957, issue of *JALCA*.

T. S. KRISHNAN received his bachelor's degree in leather technology from the University of Madras and worked as a foreman in several Indian tanneries. He joined the Central Leather Research Institute, Madras, as a Research Assistant in December, 1954.

MARK M. LUCKENS was graduated from Columbia University with majors in chemistry, biology, and education. He received his graduate training in environmental sanitation and public health, as well as industrial hygiene and toxicology, at the College of Engineering and the Institute of Industrial Medicine of New York University. As an officer during World War II, he served as a sanitary engineer, chief of laboratory services, and as director of the laboratory school of the Army. He has taught sanitary sciences and the treatment of industrial wastes at several colleges. At present, he is director of Emmet Technical Associates and is a consultant in air and water pollution control and the treatment of industrial waters and wastes, as well as in industrial hygiene and toxicology.

DR. Y. NAYUDAMMA.—See the February, 1957, issue of *JALCA*.

Cattle grubs cost the U. S. livestock industry nearly $200 million every year. The best treatment says USDA, is to spray the animal with rotenone. This works topically to kill the grubs, but not before they have damaged the animal's flesh and hide. USDA is now studying two experimental phosphate insecticides that show promise of being effective systemically. Most promising, says USDA, is Dow ET-57--*o,o*-dimethyl-*o*-2,4,5-trichlorophenyl phosphorothioate. It can be given as a drench or a pill. Radioactive ET-57 (above) was given to cattle to determine residues remaining in tissues and milk, rate at which the chemical is eliminated, how it travels in the animal, and how it kills grubs. Two apparent drawbacks: ET-57 should not be given to beef animals less than 30 days before slaughter or to dairy cattle if their milk is to be sold. The other insecticide, about which less is known, is Bayer 21/199–3-chloro-4-methyl-umbelliferone,*o,o*-diethyl thiophosphate. Neither is available commercially.

—*Chemical Engineering News*, Feb. 11, 1957.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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CONGRESSMAN JUDD TO ADDRESS FIFTY-THIRD ANNUAL MEETING

The Convention Committee has been fortunate enough to secure an outstanding speaker, with a national and international reputation as a student and actor in world affairs, to address the annual banquet at the approaching annual meeting. He is the Honorable Walter H. Judd, Member of Congress from the Fifth (Minneapolis) Congressional District of Minnesota since 1942.

WALTER H. JUDD, M.C.
Convention Speaker

Congressman Judd, a native of Nebraska, worked his way through the University of Nebraska with time out for service in the artillery in the first world war. He then studied medicine, and won a fellowship in surgery at the Mayo Clinic. For fourteen years he worked as a medical missionary in various parts of China. After first-hand observation of the communist movement in China, and after the Japanese invasion of that unfortunate country in 1937, he returned home to spend the next two years speaking throughout the United States in an attempt to arouse the American people to the menace of Japanese military expansion and the threat to world peace of communist subversion in China.

Dr. Judd practiced his profession in Minneapolis in 1941-42. In the latter year he was elected to Congress, and has been reelected seven times since. He is an influential member of the Foreign Relations Committee, and has sponsored or supported much legislation to assist industrially backward nations and promote mutual security and world peace. His talk to our Association will deal with some vital phase of current international affairs and American foreign policy.

FIFTY-THIRD ANNUAL MEETING
LAKE PLACID CLUB, NEW YORK, JUNE 2–5

PRELIMINARY PROGRAM

Sunday — June 2

Afternoon — Technical Committee Meetings
6:15 — 7:15 P.M. — President's Reception
7:30 — 8:30 P.M. — Buffet Dinner
9:00 — 9:30 P.M. — Showing of Lake Placid Club Movie
9:30 P.M. — Dancing

Monday — June 3

9:00 A.M. until noon — Registration followed by Technical Session
Afternoon — Men's Golf Tournament
6:30 — 8:00 P.M. — Dinner
9:00 P.M. — Cabaret Entertainment, followed by Dancing until midnight.

Tuesday — June 4

9:30 A.M. until noon — Technical Session
Lunch
2:00 — 4:30 p.m. — Technical Session
6:30 P.M. — Annual Banquet
Speaker: Congressman Walter Judd

Wednesday — June 5

9:30 A.M. until noon — Technical Session
Lunch
2:00 P.M. — Council Meeting

LADIES' PROGRAM

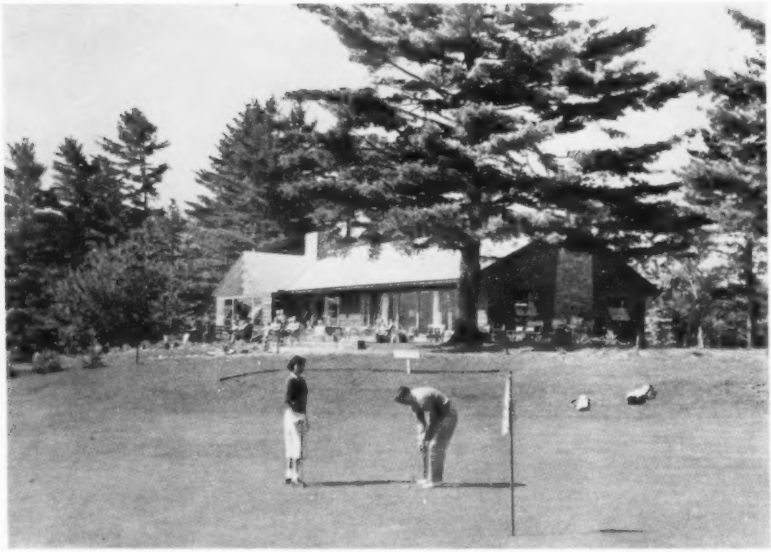
Mrs. Harold Bernard, *Chairwoman*

Monday — June 3

9:00 A.M. — Registration
10:00 A.M. — Trip to Whiteface Mountain
10:00 A.M. — Golf Tournament — 9-hole course
1:00 P.M. — Luncheon — Main Clubhouse
2:30 P.M. — Bridge and Canasta Party
2:30 P.M. — Boat Trip on Lake Placid
4:30 P.M. — Tea — Garth Lounge

Tuesday — June 4

10:00 A.M. — Putting Tournament
11:00 A.M. — Golf Tournament — Upper 18 Course
11:30 A.M. — Boat Trip on Lake Placid
1:00 P.M. — Luncheon at Golf House
2:30 P.M. — Bridge and Canasta at Golf House
4:30 P.M. — Tea at Golf House — Awarding of Prizes.



LAKE PLACID CLUB IN THE ADIRONDACKS, SITE OF THE ANNUAL MEETING OF ALCA JUNE 2–5

The Golfhouse and 18th green of the Upper Long Course

THE COVER

Olney Hall, pictured on this month's cover, houses the Department of Leather Engineering of Lowell Technological Institute, Lowell, Massachusetts. Established in 1950, the Department offers the only four-year undergraduate course in the United States leading to the Bachelor of Science degree in leather engineering. The Master of Science degree is also conferred.

At present a score of students are enrolled in the leather course. Dr. Albert E. Chouinard, head of the Department and William E. Dooley, instructor, plus a group of special lecturers from industry, give instructions in both the theoretical and practical aspects of leather engineering. Mathematics, physics, mechanics, basic chemistry, social sciences, and the humanities—the general educational background of the future leather engineer—are taught in other areas of the Institute.

Lowell Tech, founded in 1895, is a state-operated engineering college offering highly specialized technological courses in the fields of paper, plastics, electronics, and textiles, as well as in leather. Enrollment will be well over 1000 in September. This year 27 countries are represented in the student body.

Both Dr. Chouinard and Mr. Dooley are members of ALCA. In addition, the Industry Advisory Committee to the Leather Engineering Department includes other men well known to the Association. They are:

Dominic Meo, *Chairman*, Salem Oil and Grease Co.
Malcolm N. Battles, A. C. Lawrence Leather Co.
Erhard Buettner, Pfister and Vogel.
Charles T. Cares, John Flynn and Sons.
Lawrence Jones, Willard Helburn, Inc.
Louis E. Stahl, Stahl Finishing Co.

JOINT ALCA-ASTM COMMITTEE ON LEATHER

COMMITTEE ON MEASUREMENT OF WATER RESISTANCE

The committee met on February 19, 1957.

There are 6 machines in use currently for measuring the water resistance of side leather: (1) the Maeser machine, (2) tap tester, (3) Sylflex tester, (4) Hopton tester, (5) "Goosante", and (6) the Battelle-Maeser tester. Each machine will be evaluated by at least two members of the committee, using heavy and medium-weight side leather.

Subcommittees were appointed to gather pertinent methods for testing the water resistance of sole leather (J. R. Kanagy, Chairman), garment leather (A. E. Chouinard, Chairman), and glove leather (C. W. Mann, Chairman).

J. A. Bassett
Committee Secretary

ABSTRACTS

The Effect of the Interfibrillary Material on the Drying of Animal Skin. D. R. Cooper and R. L. Sykes. *J. Soc. Leather Trades' Chemists*, **40**, 401–407 (1956).—A method of hide curing which does not denature the globular proteins is desirable. Freeze-drying as a means of curing was investigated and compared with air-drying at room temperature, infrared lamp-drying, and an acetone dehydration technique. The apparent densities determined on fresh hide after drying were 1.25, 1.21, 0.86, and 0.53 respectively for air, infrared, acetone, and freeze-dried specimens. The effect of drying technique on the rehydration of hide, NaCl-treated hide, and $NaCl+Ca(OH)_2$-treated hide was studied. Freeze-dried specimens in the latter category rehydrated to completion. High and rapid water absorption tended to be associated with a low apparent density of the dried hide. Freeze-drying of salt-extracted and limed stock might provide a source of new soling material. J.M.C.

Chromatography of Large Peptides. J. Feitelson and S. M. Partridge. *J. Biochem.*, **64,** 607–612 (1956).—An ion-exchange reagent designed specifically for the chromatographic separation of large peptides is described. The reagent was prepared by applying a thin coating of a lightly cross-linked styrene polymer to a diatomaceous earth and subsequently sulfonating the resin film. Performance of the reagent was tested in relation to the isolation of a large acidic peptide from the products of trypsin digestion of the "B" chain of oxidized insulin. J.M.C.

The Technical Characteristics of Chamois Leathers for Cleaning and Filtering Purposes, and Particularly of Those Produced from the Skins of Chamois (*Rupicapra Europaea L.*). R. Airoldi. *Ann. chimica,* **45,** 517–25 (1955).—Degrained sheepskins tanned with marine oils are commonly called "Chamois leathers". The most important specifications for these leathers are (values calculated on dry basis): ash max. 5%; fatty matter (extraction with $CHCl_3$, or successive extractions with petroleum ether and a mixture of ethanol and ethyl ether) max. 5%; water-soluble matter (at 45°C.; after the fat extraction) max. 1%; pH (2 g. leather in 100 ml. H_2O) 3.5–8.0, and max. difference index 0.7 if the pH is less than 4.5; shrinkage temperature min. 60°C.; tensile strength min. 1 kg. per sq. mm. section; stretch min. 40%; water absorption min. 130% in 5 min. and 170% in 30 min. The filtration test is made by filtering gasoline mixed with 5% water through a leather disk of 20 cm. diameter: at least 750 ml. gasoline should pass through the filter before the first drop of water. It was sometimes affirmed that the chamois leather obtained from the skins of the "true" chamois (the antelope) is better than that obtained from the skins of other animals, particularly goat- and sheepskins. Approximately 1 million chamois (animals) live in Europe, and not more than 50,000 skins yearly are tanned (as chamois leather); generally these skins are very poor, with scars and various alterations. Some experiments were made with skins of chamois, goat and sheep, tanned in the same way with cod-liver oil; the chamois and goat skins absorb oil more slowly than the sheepskins. The leathers were analyzed with the standard methods, and the results showed no difference in the three different types. A sure identification of the "true" chamois skin appears to be possible neither by chemical analyses nor by microscopical examination. Taking into account the observed results, the preference for "true" chamois leathers over those obtained from goat- or sheepskins is not justified. G.A.B.

Determination of the Sulfate Ion with the Complexons. A. Casini. *Ann. Chemica,* **46,** 697–702 (1956).—The solution to be examined should contain 0.05–0.2 g. of SO_4 ion in 100 ml. and be free from buffer salts and weak acids.

(I) Determination in the presence of ammonium or alkaline salts: To 100 ml. of heated solution add an excess (20–40 ml.) of 0.1*M* solution of barium chloride ($BaCl_2 \cdot 2H_2O$), and let a = no. of ml. employed; $BaSO_4$ precipitates; boil the solution (with the precipitate) for 1–2 min., and after cooling (the solution has pH 4–6), add 3 drops of α-naphtholphthalein solution (0.1% in 70% ethanol), and titrate without filtering with 0.1 *M* Complexon, until the color turns from pink to greenish-blue. The Complexon solution is prepared following Schwarzenberg and Biedermann (*Helvetica Chim.Acta,* **31,** 459

[1948]): 37.21 g. of Complexon III is dissolved in 1000 ml. of 0.2 *M* NaOH (CO_2 free) solution; keep in polytene bottles to avoid corrosion of glass. Note that the pink color appears only a few ml. before the color change to the greenish-blue. Let b = no. of ml. employed in the titration; the result is calculated with the formula: g. SO_4 ion in 100 ml. sample = 0.0096066 $(a - b)$.

(II) Determination in the presence of alkaline-earth salts: Make a first titration as indicated above, but without heating and without addition of the barium chloride solution. Let a = no. of ml. of the Complexon solution employed. To another portion of 100 ml. of the solution to be examined add the barium chloride solution (b ml.), boil without filtering, and titrate with the Complexon solution as above. Let c = no. of ml. of the Complexon solution employed in this second titration. The result is calculated as follows: g. SO_4 ion in 100 ml. sample = 0.0096066 $(b - c + a)$. G.A.B.

Provisional Methods of Analysis Used at the Experimental Station for the Leather Industries of Naples (Italy). *Cuoio, Pelli, Mat.Concianti*, **32,** 89–115, 180–215, 271–96, 402–18 (1956).—Methods for the determination of the following physical and mechanical properties of leather are described in detail: sampling, conditioning, thickness, area, specific gravity (apparent), tensile strength, stretch, tongue tearing strength, split tear, buckle tear, stitch tear, hardness, rigidity, compressibility, abrasion resistance, resistance of the grain to compression; permeability to air, to water vapor, to water (both at constant and at variable pressure); water absorption, heating test, shrinkage temperature, gelatinization temperature, resistance to rubbing, resistance of the dyes to water (cold and warm) and to artificial perspiration, washing test, filtration test (for chamois leather), aging damage test. G.A.B.

The Firmness of Leather. E. Simoncini. *Cuoio, Pelli, Mat.Concianti*, **32,** 390–402 (1956).—The firmness or rigidity of leather is defined as the resistance to deformation under the action of external forces, and it is the converse of flexibility; however the various terms of firmness, rigidity and hardness are frequently confused. The determination of rigidity may be made with an apparatus for measuring flexibility, e.g., the Olsen apparatus (cf. MacLaughlin and Theis, *Chemistry of Leather Manufacture*, 1945, page 774), and the rigidity factor is calculated with the formula $F = \frac{M \cdot a \cdot L}{100\,(l \cdot S^3 \cdot h)}$, where M = pendulum mass, L = length of the arm, a = angle read on the scale of the moments, h = angle of bend, S = thickness of the sample, and l = breadth of the sample. With this apparatus several determinations were made on vegetable and chrome leathers, and it was shown that a previous wetting of the leather samples decreases the rigidity of the chrome leathers, while with the vegetable leathers the action is not constant. G.A.B.

The Future of the Leather Industry. F. O'Flaherty. *Shoe and Leather Reporter*, **284,** No. 6, 21 (1956).—A brief discussion of research on amino acids, solvent processing, applied research, perspiration-resistant leather, beamhouse processing, industry group research, finish research, and by-product utilization as means of producing a better product and a profitable future for the leather industry. J.J.

Leather Impregnation with Polysulfide Liquid Polymers for Hydraulic Packing and Oil Seals. K. R. Cranker. *Leather Mfr.*, **73,** No. 12, 42 (1956).—Two processes are outlined for getting complete penetration, and one process for partial penetration, of polymer into the leather. The optimum conditions for the different processes are discussed in detail. J.J.

Basic Tanning Principles for Making Sound Leather: Enzymes May Replace Lime-Sulphide. W. Petrie. *Leather Trades Review* **122,** 511 (1956). —The author describes well tanned sole leather as one that "resists water penetration and abrasion, and therefore wears well; is capable of being molded to a comfortable shape; ventilates and insulates and has the balanced rigidity and flexibility to allow easy walking." He believes a perfectly controlled enzyme process may replace the sulfide-liming process and give hides that are better prepared to make well tanned sole leather more economically than it has been made in the past. J.J.

Procollagen as a Component of Collagen Fibers. I. Banga, J. Balo, and D. Szabo. *Acta Physiol.Acad. Sci. Hung.*, **9,** 61–72 (1956) (in English); *Chem. Abstr.*, **51,** 511*e*.

Proteins and Their Degradation Products. XII. The pH Dependence of the Reaction of the ε-amino Groups of Lysine with Dinitrofluorobenzene (DNFB) in Gelatin. K. Heyns and G. Wolff. *Hoppe-Seyler's Z. Physiol. Chem.*, **304,** 200–206 (1956); *Chem. Abstr.*, **51,** 519*d*.

Utilization of Humus and Lignin. I. Preparative Study of Tanning Materials. B. Rokusho and S. Kamiya. *J. Agr., Chem. Soc. Japan*, **30,** 245–48 (1956); *Chem. Abstr.*, **51,** 748*g*.

The Effect of Steam on Wool Fiber Properties. C. H. Nicholls. *Australian J. Appl. Sci.*, **7,** 365–70 (1956).—Wool samples previously brought to equilibrium with solutions at pH values of 4, 7, and 9.8 and then dried, were exposed to steam at temperatures from 100° to 117°C. for 15 to 120 min. The steamed wools were tested for breaking load, elongation at break, abrasion resistance, and fabric reflectance, and were analyzed for alkali solubility, thiol S, and disulfide S. The acid-treated wool showed little deterioration except when steamed at 117° for more than 30 min. The deterioration of neutral wool was more marked, and that of alkaline wool was appreciable under all conditions studied. Deterioration was in close agreement with decrease of disulfide groups. Formation of thiol groups was insignificant. Alkali solubility increased little, indicating lack of action on peptide bonds. H.B.M.

Chemical Studies on the Liming of Animal Skin. VI. Effects of Organic Nitrogen Compounds in Accelerating the Unhairing of Animal Skins by Lime Liquors. Part 1—Amines. H. Toyoda and A. Fukami. *Repts. Gov. Chem. Ind. Research Inst. Tokyo*, **51,** 429–36 (1956) (English summary). —The accelerating action of various amines, in *M* concentration in lime liquor at 25°C., on the unhairing of goat and cattle hide, was studied by measuring the depilation load (Lennox, *JALCA*, **41,** 91 [1940]). The most active compound studied was diethylamine. Next came dimethylamine, ethylamine, and methyl-*n*-

butylamine. Cyclohexylamine, monoacetylethylenediamine, and N,N-diethylethylenediamine were least effective. Tertiary amines and aromatic amines were without action. The introduction of negative groups, such as acetyl and phenyl groups, into the amine molecule decreases the unhairing power markedly. H.B.M.

Photometric Determination of Aliphatic Amines. H. Hershenson and D. Hume. *Anal. Chem.*, **29,** 16 (1957).—Aliphatic amines added to an alcoholic solution containing an excess of cupric chloride produce a color having a characteristic zone absorption in the near infrared (750 to 950 mμ). The direct method, used when the amine is free of inorganic salts and/or large amounts of water, requires only that the amine be mixed with cupric chloride and diluted with absolute ethyl alcohol. If interfering substances or substantial amounts of water are present, the amine is first extracted by chloroform. The photometric determination of the amine by either method is made at the 860 mμ absorption band. A single calibration curve serves as a standard for various amines. H.R.W

Quantitative Determination of Reducing Sugars and Sucrose Separated by Paper Chromatography. R. Shallenberger and R. Moores. *Anal. Chem.*, **29,** 27 (1957).—Sugars, which have been separated chromatographically, can be determined by a simplified procedure in which each sugar is extracted from the spot cut out of the filter paper in a test tube and determined colorimetrically. Sucrose is determined after hydrolysis with invertase. Interferences caused by the filter paper are corrected for by a blank paper of the same size. The method is recommended for routine analyses of plants and foods. H.R.W.

Separation of Iron from Aluminum by Precipitation of Ferric Periodate from Homogeneous Solution. L. Ginsburg, K. Millar, and L. Gordon. *Anal. Chem.*, **29,** 46 (1957).—Iron (III) can be quantitatively precipitated from homogeneous solution as the periodate in very dilute nitric or sulfuric acid, filtered, and converted to ferric oxide by ignition. Iron may be separated quantitatively from small amounts of aluminum by this method in a single precipitation, but if the latter is present in larger ratios a two-stage precipitation is more effective. H.R.W.

Titration of Sulfate Following Separation with Alumina. J. Fritz, S. Yamamura, and M. Richard. *Anal. Chem.*, **29,** 158 (1957).—A sulfate solution is passed through a column of activated alumina, which is then washed with dilute acid. The sulfate is eluted from the column with dilute NH_4OH, then passed through a cation exchange resin column, and finally titrated with 0.01*M* barium perchlorate, using a special indicator. Sulfur in organic compounds can be determined by use of this method after a peroxide bomb combustion. H.R.W.

The Depilation of Sheepskins with Acetic Acid. M. S. Currie, J. B. Moore, and J. S. Chisholm. *New Zealand J. Sci. Technol.*, **38B,** 19–30 (1956).—Diastase was found to have no wool-loosening action, under sterile conditions, in phosphate buffer at pH 6.6 and 37°C. Pectinase produced moderate wool loosening in phthalate buffer at pH 4 and 37°C., and very marked loosening

under the same conditions in acetate buffer. The discovery that equal loosening took place in the acetate buffer without the enzyme led to a re-examination of dewooling with acids. In small scale experiments, satisfactory wool loosening was obtained with 0.05 *M* acetate buffer at pH 4 and 37°C. in 16–20 hr., or by a 45-min. soak in 0.5 *M* acetic acid, followed by wringing and storage at 32°C. for 22 hr. Other organic acids gave some loosening but were less effective than acetic. Tests with ammonia confirmed previous reports that the unhairing action is inadequate for commercial wool pulling, and decreases with time because of excessive swelling. Attempts to loosen the wool with acids at room temperature were unsuccessful. When the procedure that worked well on small pieces was applied to whole skins, patches of tight wool remained. Both the acid-treated pelt and the wool deteriorated on storage, even though the pelt was pickled and the wool was washed. H.B.M.

The Problem of Grain Crackiness in Semichrome Upper Leather. P. S. Venkatachalam. *J. Leather Technologists' Assoc. (India)*, **4,** 152–56 (1956).—The leather referred to is E.I.kip, stripped and retanned with Cr. If the vegetable-tanned stock is cracky, this fault cannot be overcome in the subsequent treatment. Causes for crackiness include insufficient opening up of the fiber bundles; deposition of too much interfibrillary material, especially on drying; weakening of the grain fibers by improper chemical treatment; and sticking of the fibers on drying. The last-named cause can be avoided by fatliquoring, or for sole leather by the use of glucose and Epsom salt, which coat the fibers. Proper drying is of utmost importance. Stripping before retanning is best done with acetone-water mixture, which gives a product containing less water-soluble material than alkaline stripping; the latter also causes excessive deposition of Cr in the grain layer. Excessive fixation of Cr in retanning also induces crackiness; 2 % Cr_2O_3 in the leather is enough. Use of cationic fat liquors has proved to be helpful. H.B.M.

The Shrinkage Temperature of Chrome Leather. D. Guha. *J. Leather Technologists' Assoc. (India)*, **4,** 157–60 (1956).—A general discussion. H.B.M

Improvement of Raw Hides and Skins. B. N. Soni. *J. Leather Technologists' Assoc. (India)*, **4,** 103–6 (1956).—A general account of methods for reducing damage by warble fly grubs, ticks, and hide beetles. H.B.M.

Problems of Insect Damage during Storage of Hides and Skins. S. C. Nandy. *J. Leather Technologists' Assoc. (India)*, **4,** 112–17 (1956).—The hide beetle (*Dermestes maculatus*) is described, and its life cycle is outlined. This insect is believed to secrete collagenase. Thorough salting of skins affords a measure of protection. Control by spraying or dusting the hides with various chemicals is discussed. Gammaxane is, at present, the most efficient. H.B.M.

The Application of Synthetic Leather Oils. D. Ramaswamy, Y. Nayudamma, and B. M. Das. *J. Leather Technologists' Assoc. (India)*, **4,** 117–19 (1956).—Kerosene was treated with H_2SO_4 to remove aromatics, dried, and chlorinated at 50°C. to contain 40% Cl. Free Cl_2 was removed by aeration, and

HCl by treatment with K_2CO_3. The product was stable. Good emulsions were obtained with (1) sulfamido acid, (2) a commercial nonionic agent, and (3) a sulfated higher alcohol, but 25–30% of the emulsifying agent was required. These emulsions were used to fatliquor Cr-tanned side leathers. The resulting leathers were softer, looser, and less full than controls treated with a conventional fatliquor, but did not feel greasy, and were very strong. The looseness may be due to the excessive proportion of emulsifying agent. This fatliquor seems especially well suited to glove and garment leather. H.B.M.

Sulfation of Nonedible Indigenous Marine and Vegetable Oils. V. R. Kishore. *J. Leather Technologists' Assoc. (India)*, **4**, 119–23 (1956).—The use and preparation of sulfated oils are discussed, and recipes are given for sulfating sardine, pongam, tobacco seed, and cottonseed oils. H.B.M.

Studies in Chrome Liquors. V. S. Padmanabhan. *J. Leather Technologists' Assoc. (India)*, **4**, 125–28 (1956).—A qualitative study was made of the acids and aldehydes produced when $K_2Cr_2O_7$–H_2SO_4 mixtures were treated with glycerol, glucose, or sucrose, employing 100 to 200% of the theoretical quantities required for reduction. The theoretical basicity of the reduced liquor was 33%. Volatile aldehydes were absorbed in $NaHSO_3$ and CO_2 in NaOH solution. Cr was precipitated at pH 6, filtered, and the filtrate was concentrated. Application of unidimensional paper chromatography revealed only that the liquors contained about 4 acids, with close R_f values. Better results were obtained by spot tests as described by Fiegl. The following acids and aldehydes were found: (1) *glycerol reduction*, formic, acetic, oxalic, glyoxalic, glycolic, lactic acids, no aldehydes; (2) *glucose reduction*, all the above acids and also tartaric acid, formaldehyde, and perhaps other aldehydes; (3) *sucrose reduction*, same. No humic acid was found. Many other possible acids remain to be tested for. H.B.M.

Chrome Upper. N. Das Sarma. *J. Leather Technologists' Assoc. (India)*, **4**, 129–132 (1956).—A process is outlined which includes unhairing by painting, deliming with boric acid (apparently no bating), an overnight pickle to pH 3.4–3.6 followed by horsing, and tanning with a solution of a commercial Cr tanning compound, treated with HCOONa 24 hr. before use. After coloring and fatliquoring, the leather is retanned lightly with a syntan (Baykanol G). H.B.M.

Finishing of Upper Leather. B. Dasgupta. *J. Leather Technologists' Assoc. (India)*, **4**, 141–43 (1956).—A brief general description, particularly of finishing buffed leathers with resin finishes. H.B.M.

Outline of Chinese Techniques of Chrome Leather Manufacture. J. K. De. *J. Leather Technologists' Assoc. (India)*, **4**, 148–51 (1956).—The process used by Chinese tanners operating in India is described. Unusual features include a very high acid pickle (3% H_2SO_4 for calfskins) with 8% salt in 40–50% water; tanning with a partially reduced Cr liquor (made by reducing in the presence of insufficient acid), reduction being completed in the tan drum with $NaHSO_3$; dyeing the grain by brushing before shaving; neutralizing before coloring by washing only; dyeing and fatliquoring at room

temperature; fatliquoring mainly with highly sulfated oils, employing up to 5%; application of finish to the damp leather on the tacking boards; use of a casein-shellac-pigment finish, high in shellac, plasticized with sulfated oil; glazing, staking, and ironing 3 times by hand. H.B.M.

Basic Studies on Oil Tannage. IV. Effect of Controlling Factors in Oil Tannage. M. Kubota. *Bull. Japanese Assoc. Leather Technol.*, **2,** 133–39 (1956) (English summary).—In tanning hide powder with oleic acid, fixed aldehyde was constant at 22 mmoles per kg., and T_s was constant at 54°C. for 5 days. Optimum H_2O content was 50–60%. Dihydroxystearic acid has slight tanning action. Fixed aldehyde in oleic acid tannage increases at alkaline pH values and in the presence of $KClO_4$ or benzoyl peroxide. Much better tannage was obtained with rice oil, with respect to fixed aldehyde and T_s. The I_2 value and ester value of the oil decreased, and acid value, peroxide value, and hydroxyl value increased as tannage proceeded. Combined aldehyde and T_s increased in the presence of Cu or Co salts, especially the oleates, and in the presence of inorganic oxidizing agents. However, with very strong oxidants, e.g., $KMnO_4$ or ammonium persulfate, T_s did not increase in proportion to increase of fixed aldehyde. H.B.M.

Microscopical Studies on Wool Dyeing: Preparation and Use of Longitudinal Sections. H. E. Millson. *Dyes Tech. Bull. No. 845, Am. Cyanamid Co.* (undated).—Descriptive. H.B.M.

Studies on the Tanning Properties of Chrome Liquor Prepared from Organic Reducing Agents. IV. Influence of Aging upon the Masking Effect of Various Organic Acids. Y. Sakimoto and T. Osugi. *Mem. Fac. Agr. Hokkaido Univ.*, **2,** 195–201 (1956) (English summary).—Cr alum solutions were treated with 0.25 and 0.5 mol organic acid ($HCOOH$, CH_3COOH, $(COOH)_2$) per mol Cr and aged. Determinations were made of pH, hot and cold basicities, and amounts of HCl reacting with hydroxo groups of the Cr complex. On aging, pH values increased in the presence of the organic acids and declined in their absence. Basicity increased in the presence of organic acids, especially oxalic, and was unchanged in their absence. The calculated amounts of acido groups entering the Cr complex declined in the order: oxalate, formate, acetate. The uptake of HCl by hydroxo groups decreased with aging in the presence of 0.25 mol formic and acetic acids, was constant in the absence of organic acids, and increased in the presence of 0.25 mol oxalic acid. In the presence of 0.5 mol organic acid, the uptake of HCl increased for all the acids, decreasing in the order: oxalic, acetic, formic. H.B.M.

Adhesion of Finish to Upper Leather. G. L. Amos and G. W. H. Thompson. *J. Soc. Leather Trades' Chemists*, **41,** 23–32 (1957).—Results are given of experiments designed to establish a quantitative estimate of the adhesive force between a leather surface and attached layers of finish. A technique is suggested which gives good reproducibility and does not require highly skilled operators. A strip of leather is cemented firmly to a glass microscope slide so that one end of the test strip, to which a load can be applied, overlaps the edge of the slide. The load required to remove the test piece gives the force required to break the bond between finish and leather. The procedure is recommended

for routine checking of production lots and may be used as a research tool to assess modifications in processing and finish formulations. Adhesion values are affected by sampling position. Data are given to show that types of binders, degree of grain correction, nature of dyes, degree of retannage, ammonia concentration in bottom finish layers, and protein content of finish formulations significantly affect adhesion of finishes to various kinds of leathers. J.M.C.

The Swelling of Hide Substance under the Influence of Liming Chemicals. A. Küntzel and E. Heidemann. *Das Leder*, **7**, 217–29 (1956).—Liming serves both to loosen the hair and to "open up" the hide. It not only dissolves keratin but also chemically changes the undissolved collagen. The "opening" of the hide is the result, principally, of swelling and deswelling. Swelling can be measured satisfactorily and was therefore used in this study of opening and loosening of the hide fiber structure by liming agents. Photomicrographs showed that swollen hide fibers in a section were not in as close contact as before swelling and that this separation remained after deliming. A chemical change has occurred because hide powder made from limed hide is softer and woolier than powder made from untreated, fresh hide. Solution of the material between the hide fibers might be considered the cause of opening up of the hide, but the amount of this material going into solution is extremely small. During swelling the fibers thicken, contract, and increase in volume. Maximum swelling can be observed only on individual fibers, because fiber weave restricts the contraction of the fibers and the sheath restricts thickening. The experimental hide material consisted of "cubes" (15×18 mm.) cut from the middle split of an acetone-dehydrated bull hide. Two g. portions (10 pieces) were treated for 3 days in closed vessels with 20 ml. of the liming solution at 2 temperatures, 10° and 25°C. After 3 days the pieces were removed with pincers, blotted on filter paper, then weighed. The swollen weight was calculated as percent of the original dry weight. Alkalinity of the solutions before use was determined by titration under nitrogen with 0.1 *N* HCl and phenolphthalein. The pH value was measured under nitrogen with an alkali glass electrode and correction was made for "sodium error" if Na^+ was present. Calcium was determined either as oxalate after oxidation with Br_2 or, if sulfides were absent, by titration with Komplexon III. The used liquors were not analyzed because of the presence of protein and excess lime. Results are given in tables and also curves plotting swelling against salt concentration. Pure alkali is taken up by carboxyl groups with discharge of the basic NH_3^+ groups so that the collagen becomes a high molecular polyanion in which the charged groups show electrostatic repulsion for each other. Because of peptizing action in alkali, swelling does not show a sharp maximum as in acid solutions. Addition of a common cation, e.g., NaCl to Na_2S solutions, decreases swelling because the NaCl represses dissociation of the sodium collagenate by mass action. The decrease in hydrolysis and lowering of pH have minor influence. Lime swells hide much less than an equivalent solution of alkali hydroxide. Addition of salt (NaCl) to a lime solution results first in an increase in swelling followed by a decrease as the amount of salt increases. Increased swelling results because of the formation of sodium collagenate from calcium collagenate and is not related to the increase in solubility of lime caused by addition of salt, because if that were true, the maximum swelling should be in *N* NaCl instead of in 0.2–0.3 *N* NaCl. At higher salt concentrations the ionization of the collagenate is decreased and therefore swelling decreases. Calcium chloride does not form collagenate but

causes hydrotropic swelling similar to the action of urea or thiocyanate. Undissociated $CaCl_2$ molecules, with their water sheath, attach to the peptide groups of collagen, disrupting the hydrogen bonds that hold the peptide chains together. Addition of increasing amounts of $CaCl_2$ to a Na_2S solution causes a sharp decrease in alkalinity and in swelling to a minimum in 0.4–0.8 *N* $CaCl_2$, followed by a slight increase in swelling at higher concentrations. When $CaCl_2$ was added to a Na_2S solution, a white precipitate formed which was about 90% $Ca(OH)_2$ and 10% CaS; the sulfide concentration of the solution was therefore lowered. The addition of a small quantity (0.1–0.2 *N*) of $CaCl_2$ to a lime solution decreased hide swelling because addition of Ca^{++} decreased the solubility of lime. After the initial decrease, increasing amounts of $CaCl_2$ increased swelling continually because of its hydrotropic swelling action. Addition of increasing amounts of Na_2S to a lime solution results in a swelling curve similar to that for sulfide alone but which is higher (greater swelling) because the lime reserve maintains alkalinity. Stirring was important; for example there was 267% swelling in a still liquor and 281% in one that was stirred. In the ternary systems, lime and Na_2S with increasing amounts of either NaCl or $CaCl_2$, the swelling curves were essentially the same as those for sulfide without lime; only a minor role was played by lime. I.D.C.

A Critical Review of the Literature of 1955 on Sewage, Waste Treatment, and Water Pollution. H. Heukelekian, *Chairman, etal. Sewage and Industrial Wastes*, **28,** 707 (1956).—Mathis [*Bull. Centre Belge Etude et Doc. Eaux* (Belgium), **5,** 87 (1954); *Water Pollution Abstr.* (Brit.), **28,** 101, 675 (1955)] determined the effectiveness of screening, settling, and centrifuging for treating waste waters from softening, depilation, and fleshing of skins. Centrifuging was most effective but not practical on a large scale. Various methods of further treatment by chemical means were also investigated. These methods included chlorination, coagulation with ferric sulfate, and removal of sulfides by acidification with sulfuric acid. Schlichting [*Leder*, **5,** 214 (1954); *Pub. Health Eng. Abstr.* **35,** 10, 20 (1955)] describes tests in which tannery effluents after settling were mixed with activated sewage sludge. Toxicity tests were made by the addition of reacted liquor to aquarium fish. It was found that when 1.5 gal of effluent were mixed with 150,000 gal. of sludge, the product was nontoxic after 14 days. J.F.W.

Nature of the Tannins in *Terminalia Chebula*. K. J. Scaria, S. K. Barat, and B. M. Das, *Bull. Central Leather Research Inst., Madras*, **3,** 70–75 (1956).—Ground myrobalan nuts were extracted with acetone. The extract was evaporated, redissolved in water, and filtered to remove chebulic acid. This solution was extracted with ethyl acetate in a special countercurrent extractor for 1 week, first at pH 7 (Fraction 1), and then at pH 1 (Fraction 2). The residual aqueous solution was evaporated and the residue redissolved in methanol (Fraction 3). Each fraction was evaporated and redissolved in water. Titration curves were obtained for each fraction, as prepared and after boiling under reflux for 1 week to induce hydrolysis. The titration curves for Fraction 2 (the largest fraction) closely resembled that of whole myrobalan extract; those for Fractions 1 and 3 showed that these fractions are less buffered. None of the titration curves was much affected by hydrolysis. Values are given for molecular weights and percentages of bound water for each fraction, before

and after hydrolysis, but no information is given as to how these data were obtained. The reported molecular weights, before and after hydrolysis, are: Fraction 1, 1141, 201; Fraction 2, 208, 212; Fraction 3, 125, 94. Corresponding values for bound water (in g. per g. of total solubles) were: 16, 4; 6, 0.85; 6, 16. H.B.M.

C.L.R.I. Mourns the Death of Its First Director. S. K. Barat. *Bull. Central Leather Research Inst., Madras,* **3,** 50–55 (1956).—An obituary of the late Prof. B. M. Das. H.B.M.

Spectrophotometric Studies. V. Differential Titration of Phenolic Groups of Vegetable Tanning Materials by Photometric Technique. Y. Nayudamma, A. Nagasironmani, and D. Ramaswamy. *Bull. Central Leather Research Inst., Madras,* **3,** 56–69 (1956).—The differential absorption titration technique [*JALCA,* **51,** 570, (1956); **52,** 48 (1957)] is applied to 16 commercial tannins. When differential absorption (D.A.) is plotted against volume of NaOH added, each curve consists of a series of linear segments, each terminating in a very short horizontal segment. The slopes of the linear segments decrease progressively with increasing volume of added NaOH. Each step is believed to correspond to the end point of the titration of one type of phenolic OH group. The number of different types of phenolic groups varied from 4 to 9 for the tannins studied. In most cases the titration curve became horizontal at pH 10.0–10.5, indicating that all phenolic groups had been titrated, but in 3 cases (babul, karada, and *Terminalia arjuna*) no such end point was reached. The slope of the linear segment is a qualitative measure of the ease of ionization of the phenolic group that is being titrated. The phenolic groups are classified, according to the magnitude of these slopes, into categories that are ionizable (*a*) easily, (*b*) less readily, and (*c*) with difficulty. Myrobalans, divi divi, sumac, cutch, and white valem contain *a* and *b;* mangrove and babul *b* only; avaram, *Cassia marginata, Hopea parviflora, Terminalia arjuna,* gambier, and karada, *b* and *c;* quebracho and wattle, *a, b,* and *c.* The percentages of total phenolic groups determined by the D.A. titration method agree fairly well with those previously calculated by Goldschmidt's technique [*JALCA,* **51,** 570, (1956)], except for *T. arjuna* and quebracho, for which the latter method gave abnormally large percentages. Comparison of contents of total phenolic groups, and those belonging to types *a, b,* and *c,* is helpful in predicting which tannins are interchangeable in practice. Speculations are advanced as to the role of the different phenolic group types in imparting such properties as rapid penetration, mellowness, irreversible fixation, etc. H.B.M.

Bacterial Penetration in Raw Hide during Staling. S. C. Nandy, S. N. Sen, and B. M. Das. *Bull. Central Leather Research Inst., Madras,* **3,** 76–83 (1956).—Pieces of fresh hide were washed, fleshed, and stored damp at 30°C. Sections were cut at intervals up to 3 days and were stained and examined for bacteria. During the first 16 hr. bacteria were found in the layer next to the flesh side only, gradually penetrating into the center of the corium, but at 24 hr. numerous bacteria were found at the junction of the epidermis and corium (more than in the center of the corium), which indicates penetration through the grain side. Hair slip occurred at 24 hr. Bacterial counts are re-

ported for solutions obtained by shaking pieces of hide with 10 parts of water for 2 hr. They ranged from 0.6 million per ml. after 3 hr. staling to 1.25 billion per ml. after 72 hr. About 70% of the organisms were chromogenic for all growth periods. H.B.M.

The Effect of Shell Lime on the Fiber Structure of the Pelt in Liming Cow Hides. S. K. Sarkar, S. K. Mitra, and B. M. Das. *Bull. Central Leather Research Inst., Madras,* **3,** 84–91 (1956).—Pieces of cow hide were limed for 9 days with 15% shell lime (26% available lime) or 15% of stone lime (50% available lime), alone or with the addition of 0.5% Na_2S or NaOH. In each case, weight gains with stone lime exceeded those with shell lime. The weights passed through maxima at 4 days (stone lime) and 7 days (shell lime) when NaOH was added. In the other liquors the weights increased throughout the 9 days. The stone lime gave a smoother grain, but the shell lime gave a fiber structure that was considered preferable for E.I.kip leather. H.B.M.

Isotope Exchange in Solutions of the Green Modification of the Chromium Salts. Y. A. Fialkov and Y. P. Nazarenko. *Zhur. Neorg. Khim.,* **1,** 565–78 (1956); *Chem. Abstr.,* **51,** 1759*e*.

Chromium (III) Hydroxides. A. Krause and S. Kotkowski. *Roczniki Chem.,* **30,** 11–28 (1956) (German summary); *Chem. Abstr.,* **51,** 1761*e*.

Isoelectric Point of Collagen. G. A. Arbusov. *Nauch. Trudy Moskov. Tekhnol. Inst. Legkoi Prom.,* **4,** 70–72 (1954); *Chem. Abstr.,* **51,** 2094*b*.

***In Vitro* Inhibiting Experiments on the System Collagenase of the Spinal Larvae of *Hypoderma Bovis* and Collagen.** E. Lienert and W. Thorsell. *Wein. Tierärztl. Monatschr.,* **43,** 743–51 (1956); *Chem. Abstr.,* **51,** 2104*a*.

Theory of Elastic Mechanisms in Fibrous Proteins. P. J. Flory. *J. Am. Chem. Soc.,* **78,** 5222–35 (1956); *Chem. Abstr.,* **51,** 2105*b*.

The Influence of Different Methods of Production and Treatment on Certain Molecular Properties of Casein. H. Lück and F. J. Joubert. *Milchwissenschaft,* **10,** 413–18 (1955); *Chem. Abstr.,* **51,** 2196*h*.

Utilization of Sulfite Cellulose Waste Liquors as Tanning Material. IV. Titration Curves and Absorption Curves of Various Lignin Extracts. Y. Sakimoto. *Jap. J. Zootech. Sci.,* **26,** 145–47 (1955) (English summary).—Titration curves and absorption curves as functions of pH are given for 6 lignosulfonate extracts and compared with those for typical vegetable tannins. The curves for the lignosulfonates appeared to vary with the previous treatment of the extract. **V. The Preferential Tannin Absorption by Hide Powder from Blended Tan Liquor (2).** Y. Sakimoto and K. Katayama. *Ibid.,* 149–53 (1955) (English summary).—Preferential absorption of one or the other tannin in a binary blend was measured from the gallic acid and ethyl acetate values of the liquors from which part of the tannin had been absorbed

by hide powder. Each blend was tested at its natural pH and at pH 6. The following preferential absorptions are reported: (1) wattle-mangrove, wattle, more at pH 5.8 than at 4.3; (2) quebracho-wattle, quebracho, especially at pH 6; (3) quebracho-mangrove, quebracho, especially at pH 4.1; (4) wattle-lignosulfonate, wattle (slight) at both pH values; (5) quebracho-lignosulfonate, quebracho at both pH values; (6) wattle-chestnut, chestnut (slight). **VI. Preferential Tannin Absorption from Blended Liquors (3).** Y. Sakimoto and K. Katayama. *Bull Japan Assoc. Leather Technologists*, **2**, 146–51 (1956) (English summary).—Pieces of limed, dehaired, and delimed horsehide were partly tanned with various blends and then retanned with the same blends at 3% concentration for 3 hr., using 500 ml. liquor to 200 g. hide. Each blend was used at its natural pH value and at pH 5.5. Preferential absorption was measured by determining gallic acid values and ethyl acetate values for the spent liquors. The reported results for preferential absorption are: (1) chestnut–wattle, none at pH 3.6–4.6 or 5.5; (2) chestnut–soluble quebracho, chestnut at pH 5.5 but not at 3.7–4.4; (3) chestnut–mangrove, chestnut at pH 5.4, more than at 3.5–4.7; (4) chestnut–Hansa D (lignosulfonate), chestnut at pH 2.7–4.3 and even more at 5.5; (5) wattle–soluble quebracho, wattle at pH 4.5 and 5.3–5.7; (6) wattle–mangrove, same as (5); (7) wattle–Hansa D, wattle at pH 3.4–4.6 and 5.5; (8) soluble quebracho–mangrove, quebracho at pH 4.4–4.6 and much more at 5.3–5.6; (9) soluble quebracho–Hansa D, quebracho at pH 3.6–4.4 and 5.4–5.7. In general, preferential absorption of the natural tannin increases with pH value. Wattle is preferred to chestnut for blending with lignosulfonate. H.B.M.

Report of the VGCT Fat Commission. R. Schubert. *Das Leder*, **7**, 277–79 (1956).—Methods are given for the analysis of "water-soluble" fatliquoring materials. Water and volatile organic solvents are determined by distillation with xylene and measurement of density of the distillate. Water is determined by the Karl Fisher method. Emulsifiers are determined by the Panzer-Niebuer method. I.D.C.

Systems and Biology of Warble Flies. O. Gebauer. *Das Leder*, **7**, 273–76 (1956).—A brief description of the habits, distribution in Switzerland, and methods of combating the two kinds of warble flies, *Hypoderma bovis* and *H. lineatum*. I.D.C.

Preparation and Properties of Glucose-reduced Liquors. P. J. van Vlimmeren. *Das Leder*, **7**, 265–72 (1956).—Determinations were made of the amounts of formic and oxalic acids in glucose-reduced chrome liquors as a function of the amounts of acid and glucose and the order of addition. The following two solutions were prepared: (A) 250 g. of sodium dichromate in 375 ml. of water mixed with concentrated H_2SO_4 to give a final liquor basicity of 33.3% or 47%; (B) dichromate solution mixed with 25% or 35% of glucose on the weight of dichromate (an excess of glucose over theory from the Stiasny equation of 64% or 130% resp.). Glucose was added slowly to A and H_2SO_4 to B, after which the solutions were boiled for 25 min. to reduce all dichromate, then made up to 1 liter. Total basicity was determined by the method of Thorstensen and Theis (*JALCA*, **47**, 588); formic acid by acidifying strongly with H_3PO_4, distilling, and titrating the distillate. Oxalic acid was determined as the Ca salt as usual after first adding an excess of NaOH,

heating 30 min., and filtering. More organic acid was formed when acid was added last than when glucose was added last. Change in the amount of H_2SO_4 resulted in little change in the amount of organic acid formed. The amount of glucose had little influence on the amount of organic acid if glucose was added last, but was quite important when H_2SO_4 was added to the glucose-dichromate mixture. In the latter case an excess of glucose resulted in the formation of relatively more HCOOH. Almost all of the glucose was oxidized when 64% excess was present, but with an excess of 130% the oxidized solution contained 7–8% glucose if acid was added last, or 19–22% if glucose was added last. The tanning action of these liquors was determined on Freiberg, unchromed hide powder as follows: 5 g. of powder was soaked for 1 hr. in 50 ml. of water, treated with enough liquor to give an end concentration of 0.1 mol Cr_2O_3 per liter, then tanned for 6 hr. (except when time was a variable factor) at 20°C. in a 1:12 float. The uptake of Cr increased as either the time of tanning or the basicity of the liquor increased, but was influenced very little by the organic acid. Tests with liquors to which known amounts of formic or oxalic acids had been added showed that the former decreased Cr fixation slightly, while oxalic acid increased fixation. Calculations indicated there were minor effects caused by other oxidation products. Tests were made on skins by tanning them with 33% and 42% basic liquors, both with and without 0.5 mol of HCOONa per mol of Cr_2O_3. Instead of adding the formate just before tanning, as was done by Theis, the solutions were boiled to complete the reaction; much less formate was therefore needed. Skins to be tanned in the 33% basic liquor were pickled in 5% salt and 0.8% H_2SO_4 and those to be tanned in the 42% basic liquor in 8% salt and 1.25% H_2SO_4, so that the final pH of all tanned skins was about the same. After tanning for 7.5 hr., the skins were aged 5 days, then split into 5 layers. The Cr content of the middle layer was always higher than that of the outside layers, because there was less pickle acid in the center. The grain layer (no. 1) of skins tanned in 42% basic liquors contained more Cr_2O_3 than the no. 2 layer because of the large particle size and poor diffusion of the tanning agent through the grain. The total takeup of Cr_2O_3 from 42% basic liquors was less than that from 33% basic liquors. Addition of HCOONa decreased Cr_2O_3 uptake, on the average, from 3.85% to 3.64%. In the 42% basic liquors more Cr_2O_3 was taken up from glucose-reduced than from SO_2-reduced liquors, because the former contained oxalic acid. In general the results with hide powder and with skin were in agreement. The above results have only a limited application to practice, because the quality of leather depends on many factors other than Cr_2O_3 content. This work would indicate that either masking with formate or using a 42% basic liquor would lower leather quality, because both decrease the amount of Cr_2O_3 taken up. Practical trials show just the opposite. In Holland, formate-masked, SO_2-reduced, highly basic liquors are used with good results. Also one would expect a 42% basic glucose-reduced liquor to give better results than a SO_2-reduced liquor of equal basicity, because of a somewhat greater takeup of Cr_2O_3. At a basicity of 33% the SO_2-reduced liquor should excel, but here also practical results show the reverse. In general at a basicity of 33%, glucose-reduced liquors give a fuller leather than SO_2-reduced liquors, while at a basicity of 42% the SO_2-reduced liquors give decidedly better results, especially if the liquors are masked with formate. I.D.C.

What's New in Bio-Oxidation. Anon. *Chem. Eng.*, **64,** No. 3, 162–64 (1957).—Trickling filters for bio-oxidation of wastes may be supplanted by

oxidation towers packed with corrugated plastic or redwood chips, instead of crushed stone. Improvements in the activated sludge and aerated lagoon methods of purification are described. H.B.M.

Study of the Affinity of Black Wattle Extract Constituents. IV. Relative Affinity of Polyphenols for Swollen Chemically Modified Collagen. R. L. Sykes and D. G. Roux. *J. Soc. Leather Trades' Chemists*, **41,** 14–22 (1957).—The qualitative effect of chemical modification of collagen on the relative affinities of wattle tannin constituents was studied by column chromatography on the modified collagens, coupled with two-dimensional paper chromatography. Regardless of substrate, the polyphenols exhibited similar patterns. The over-all affinities of the tannin constituents for the different substrates increased in this order: esterified collagen, collagen, deaminized collagen, carboxymethylated collagen, and acetylated collagen. Differences in affinity between the various collagens and the wattle tannin constituents were much less marked and probably less significant than inherent differences in the relative affinities of the individual polyphenols. The predominantly hydrogen-bonding nature of the vegetable tanning process is conclusively established by the similarity in the relative affinities of wattle tannins for collagen, modified collagens, and cellulose. J.M.C.

The Influence of Acids and Salts in Sole Leather Tannage. III. Acids and Salts in the Early Tan Liquors. H. Anderson. *J. Soc. Leather Trades' Chemists*, **41,** 2–7 (1957).—The importance of acid and salt control during initial penetration of tannin is stressed in sole leather tanning. A quantitative relationship is shown between plumping and firmness, the firmness being governed by the degree of plumping of the fiber at the time it is tanned. Firmness is evaluated by the rigid pendulum method. Plumpness of grain layer fibers at the time of initial tannage influences the ultimate firmness of the leather to a degree which seems out of all proportion to the relative depth of grain and corium layers. J.M.C.

The Vegetable Tannage of Sheepskins: A Systematic Study of the Influence of Various Factors in the Tanning Process. I. Plan of Experiment and Details of the Tannages. M. F. Chambers, M. Dempsey, R. G. Mitton, and E. F. Nattrass. *J. Soc. Leather Trades' Chemists*, **41,** 7–13 (1957).—Sheepskins were vegetable-tanned after bating, and also after bating and pickling, using tan liquors of pH 2, 3, 4, and 5 and with salt contents near 0, 2, 4, and 6%. Wattle and chestnut tannins were used. After drying to crust, the skins were subsequently given firm and soft finishes. Details of the tannages are given along with enumeration of the analyses and tests performed. The results are to be described in later papers. J.M.C.

How Professor E. Stiasny Discovered Synthetic Tannins. Anon. *Das Leder*, **7,** 209–10 (1956).—Stiasny was studying the determination of acidity of tan liquors by titration. In order to see the end point, tannin was first removed with gelatin, but gelatin absorbed some acid. He was also studying the action of HCHO on vegetable tannins, especially quebracho. He observed the precipitation of tannin by boiling it with HCHO and HCl and later found that only catechol tannins were precipitated. He noted that the hide powder nontannin

solution from catechol tannins gave a precipitate with HCHO but that that from pyrogallol tannins did not; however the pyrogallol nontannin after treatment with HCHO gave a precipitate with gelatin, that is, it had been converted to a tannin. This led to a study of condensations with other materials. The patent in 1911 described both (1) condensation of HCHO with phenolsulfonic acid to form a product marketed later by BASF as Neradol D, and (2) condensation of phenol and HCHO to form a product later called Novolak, then treating this with H_2SO_4 to make it water-soluble. I.D.C.

The Spanish Chestnut in Europe. R. Sormani. *Das Leder*, **7**, 229–33 (1956).—Chestnuts (*Castanea sativa* or *C. vesca*) have been cultivated for their edible nuts from early times. They are susceptible to the ink disease (*Blepharospora cambivora*) and to the blight, although they are more resistant to blight than the American chestnut. Chinese chestnuts (*C. mollissima*) are immune to the blight, whereas there are resistant and non-resistant varieties of the Japanese chestnut (*C. crenata*). A careful survey showed the following stands in Europe: Italy, 730,000; France, 450,000; Spain, 110,000; Portugal, 80,000; Yugoslavia, 60,000; and Switzerland, 17,000 hectares (2.47 acres). In 1952 Italy, France, and Switzerland produced 63,000 tons (metric) of 100% chestnut tannin. Trees for extracting should be over 70 years old and should be stored for 2 years after cutting to reduce their moisture content from 50% to 40%. The wood contains 8% tannin; the bark more, but it is of poor quality. The following commercial extracts are made: liquid, 34%; solid, 67%; powdered (solid, ground), 71%; and spray-dried powder, 80% tannin. There are two types, natural (pH 3.5) and neutralized (pH 4.5). The uses of chestnut extract are reviewed. I.D.C.

Modern White and Glacé Leather. E. Immendörfer and A. Bauer. *Das Leder*, **7**, 210–12 (1956).—Some directions are given for making white, flexible, light-stable, washable leathers with the following BASF products: Lutan B, a highly basic aluminum chloride; Lutan O and Lipamlin licker O, cationic fat liquors; Immergan, a sulfochloride tannin; and Nekanil O extra used in washing. I.D.C.

Report of the VGCT Commission on Leather Dyes. F. Wassmuth. *Das Leder*, **7**, 233–34 (1956).—Tentative methods are given for testing the stability of anionic dyes to hard water, solubility and anionic dyes, and wood extract dyes. I.D.C.

CORRECTION

The name of the heterocyclic compound whose structural formula is given on page 8 of Vol. LII, No. 1 should be 2, 5, ethoxytetrahydrofurane, not diethyltetrahydrofurane.

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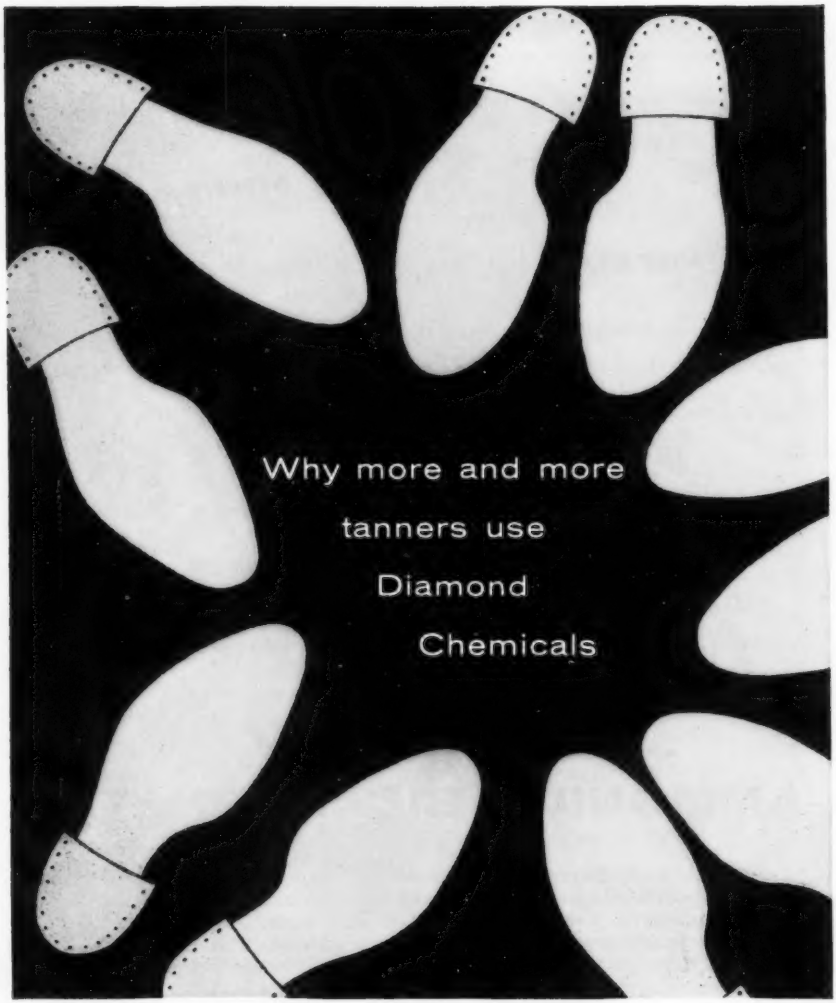

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Soluble Solids	75.50

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